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HEAD-MASTER OF THE MIDDLE-CLASS
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EDITORS' PREFACE.

NOTWITHSTANDING the large number of scientific works which have been published within the last few years, it is very generally acknowledged by those who are practically engaged in Education, whether as Teachers or as Examiners, that there is still a want of Books adapted for school purposes upon several important branches of Science. The Series of which this is the first volume will aim at supplying this deficiency. The works comprised in the Series will all be composed with special reference to their use in school-teaching; but, at the same time, particular attention will be given to making the information contained in them trustworthy and accurate, and to presenting it in such a way that it may serve as a basis for more advanced study.

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G. C. F.
P. M.

AUTHOR'S PREFACE.

THE properties of Energy and the laws which regulate its changes force themselves in some form or other upon the notice of students of almost every branch of science. There are, however, few connected and systematic expositions of these subjects within reach of the general student, and when the knowledge of them is derived exclusively from popular lectures and current text-books, he has to encounter two difficulties. The first is to avoid confounding the results of theoretical reasoning with conclusions founded simply on observation. The second and greater difficulty is to escape reasoning in a circle. Meyer's proposition, for instance, which shows the connection between the numerical values of the dynamical equivalent of heat and the two specific heats of air, is in some books used to deduce the first when the other two members are given, while in others it is employed to find the specific heat with constant volume by means of the specific heat with constant pressure, and

the dynamical equivalent of heat. Similar remarks apply to several propositions depending on the Second Law of Thermodynamics.

In the natural arrangement of the subject, the relation of Energy to Heat should follow the purely dynamical consideration of energy, not only on account of its practical importance, but because the measurements and formulæ connected with other transmutations of energy are generally determined by interposing the change into heat. Such, in fact, is the order adopted in the present text-book, which is an attempt to do for Thermodynamics what has long since been done for Elementary Dynamics. The work aims at tracing, in a systematic manner, the reasoning by which the Dynamical Theory of Heat, and its chief consequences, are established. Each chapter opens with a brief description of some experiments required either to supply the fund of observations on which the laws and theory are founded, or to show how certain constant quantities used in the calculations have been determined by careful and trustworthy physicists. Then follows: first, a discussion or examination of the experiments; secondly, the definitions of the scientific terms required for the expression of the general laws to which they conduct us; next we have the formal enunciation of these laws; and finally, the strictly logical or mathematical consequences which can be deduced from them.

It has been an object to avoid the use of advanced mathematics. In one case only has an integration to be effected (pages 64 and 130), namely, the simple case in which the sum is represented by the area bounded by a rectangular hyperbola.

The plan of gradually establishing and illustrating each part of the theory, before reasoning from it, is employed not only in each chapter individually, but in groups of chapters and throughout the whole work. For instance, in order to form the theory of Heat-Engines, we begin with the best known Heat-Engine, the Steam-Engine. Then, as a connecting link between the steam-engine and the purely theoretical engine, we have the Air-Engine.

For a fuller account of the Kinetic Theory of Gases given in the last chapter, the reader is referred to Clerk Maxwell's treatise on Heat. Within the limits of the present work it was not possible to do more than present a brief analysis of the theory and of the principal evidence in its favour.

LONDON : *September*, 1877.

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THE

DYNAMICAL THEORY OF HEAT.

CHAPTER I.

INTRODUCTION—DYNAMICAL PRINCIPLES.

IT will be convenient to state at the outset of our investigations the definitions and principles of dynamics, to which reference will subsequently have to be made.

§ 1. **Mass and Force.**—The *mass* of a body mean the quantity of matter in it.

The *momentum* of a moving body means the *quantity of motion* that it has at any instant, and is measured by the product of its mass and velocity.

A *force* is defined in dynamics as any cause which tends to produce motion.

With this definition it is evident that the natural way of measuring forces is by the quantity of motion they produce in a given time, as, for example, a second.

Let m be the mass of a body acted on by a force, and let a be the velocity produced in a second of time, then the quantity of motion produced in a second is $a\,m$.

Forces are regarded as equal when they produce equal quantities of motion in the same time; hence a force is constant when it produces the same quantity of motion in a body in every equal interval of time during which it acts.

The velocity produced in the unit of time, that is in a second, is termed the acceleration; hence equal forces are those which give equal accelerations to the same mass; and a force is constant when the acceleration is constant, in other words, when the velocity of the body on which the force acts receives equal increments in equal intervals of time.

Let F be the measure of a constant force acting on a body of mass m, and let a be the resulting acceleration, then by choosing convenient units we may write

$$F = a\,m.$$

When a body falls freely under the influence of the earth's attraction, its motion is accelerated. Here the force acting on the body is the amount of the earth's attraction on it, or what is commonly called its weight. The acceleration, which varies slightly at different places in the earth's surface, is termed the *acceleration due to gravity*, and is usually designated by the letter g. Hence, if W be the weight of a body and m its mass, the above equation becomes

$$F = W = g\,m.$$

If the mass of a body be taken as the unit of mass the equation becomes, in that case, $W = g$, that is to say, there are g units of force in the weight of a body of unit mass. Hence, if one pound be the unit of

mass, there are g units of force in the *weight* of a pound, and if the gramme be the unit of mass, there are g units of force in the weight of a gramme. When lengths are measured in feet, and time in seconds, the value of g in England is about 32·2, so that the unit of force is a little less than the weight of half an ounce; and when lengths are measured in centimetres and time in seconds, g is about 980.

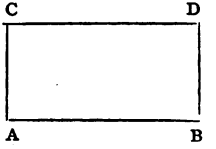
In the foot-pound-second system of units, therefore, the weight of a pound is 32·2, and in the centimetre-gramme-second system the weight of a gramme is 980.

§ 2. **Work.**—A force does work when its point of application moves in the direction of the force and the work done is measured by the product of the magnitude of the force and the distance through which the point of application moves in the direction of the force.

For example, if a body be allowed to fall from any height, the work done by the earth's attraction on the body will be found by multiplying its weight by the height. If a load be lifted through a height s, the work done by the lifting force is the weight of the load multiplied by s. If a locomotive pulling with a uniform force F, move a train through a distance s, the work done by the locomotive is Fs.

Hence, work may be represented graphically by an area. Let a force act on a body at a point A. Let A B D C be a rectangle such that A B has the direction of the force, and let A B be the space moved through. Let A C perpendicular

FIG. 1.



to A B represent the magnitude of the force, then the work done is $F \cdot s = \text{A C} \cdot \text{A B} = \text{area of A B D C}$.

Kinetic Energy.—If a body of mass m is moving with velocity V, the product $\frac{1}{2} m V^2$ is termed its kinetic energy. We shall justify the use of this term by showing that $\frac{1}{2} m V^2$ is equal to the work which must be done on the body before it can be brought to rest. We may then say that the kinetic energy of a moving body is the power it possesses to do work in consequence of its actual velocity, and when the body moves as a whole with a velocity V, it is measured by the product $\frac{1}{2} m V^2$.

When the motion of a body is uniformly accelerated the work of the force in a given time is equal to the increase of kinetic energy in the same time. This may be proved as follows :—

Let m be the mass of the body, F the force, a the acceleration or gain of velocity per second, s the space through which the body moves in t seconds, u and v the initial and final velocities respectively, then the gain of velocity is $a\,t$, but it is also $\pm (v-u)$.

$$\therefore \pm (v-u) = a\,t.$$

Also, since the mean velocity is $\frac{1}{2}(v+u)$,

$$\frac{1}{2}(v+u)\,t = s,$$

And

$$a\,m = F.$$

Multiply these three equations together:

$$\therefore Fs = \pm \left(\frac{v^2 m}{2} - \frac{u^2 m}{2} \right).$$

If the force act in the direction of motion the

positive sign must be taken, and since $\frac{1}{2} u^2 m$ is the kinetic energy of the body at the beginning of the space s, and $\frac{1}{2} v^2 m$ that at the end, we have

$$F s = \text{gain of kinetic energy.}$$

If the force act in the direction opposed to that of motion the negative sign must be taken, and

$F s = \frac{1}{2} u^2 m - \frac{1}{2} v^2 m =$ loss of kinetic energy.

If the body start from rest so that $u = o$, then $F s =$ the kinetic energy produced. If the body start with velocity u, and be retarded by a force F, then, s being the space in which it is brought to rest, that is to say, at the end of which $v = o$, we have

$$F s = \frac{1}{2} u^2 m.$$

= the kinetic energy accumulated at the beginning of the motion.

Hence, the kinetic energy generated by a force F, acting through a space s may be destroyed by the same force in the space s and the product, $\frac{1}{2} m u^2$, which we have termed the kinetic energy of the body, is the measure of the work accumulated in the body.

In the above equations we have supposed the force to be constant through the space s. If the force be variable, we may divide the space s into portions s' each so small that we may suppose the force constant through each, and to receive a slight sudden increase at the end; then for each small space s'

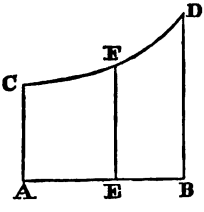
$$F s' = \text{gain or loss of energy in space } s'.$$

By adding the different portions of the work on

the one side, and the different increments of energy on the other, we arrive at the result that the total work done by the force is equal to the total increase of kinetic energy.

From this it follows that even when the force is variable the work done may be represented by an area. For example, let A B be the space through which the body moves, let A C represent the force at the beginning of this space, and B D that at the end. Let C F D be a curve such that the ordinate E F at any point F represents the force at the corresponding point of the path, then the work done is represented by the area A B D C.

Fig. 2.



When several forces act on a body or system of bodies, we may conclude, by adding their separate effects, that the whole work of all the forces equals the total increase in the kinetic energy of the body or system of bodies.

If therefore a machine is acted on by forces tending to move it, and resistances tending to hinder the motion, we have the work of the former equal to the work of the latter, together with the total increase of kinetic energy, or,

Work expended = Work done + Work accumulated.

Let a piston move in a cylinder through a distance d in consequence of a uniform pressure P, then the work done is $P d$. But if the constant pressure on the piston be p pounds per unit of area, and if

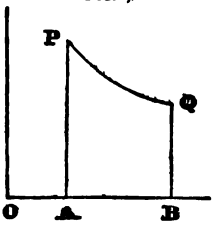
v be the volume of the space through which the piston moves, and the weight of the piston be independently supported, the work done is also $p\,v$. For, let a be the area of the piston. The whole pressure on the piston $= p\ a$; since this pressure is exerted through a distance d the work done $= p\ a\ d$. But $a\ d =$ the volume v of the space through which the piston moves. Hence the work $= p\ v$. When the surface of a body is subject to a constant pressure of p pounds per unit of area, if the body expands so that its volume increases by a small quantity v', then the work done in the expansion is $p\ v'$. For if we divide the surface into small parts, each part may be compared to a piston forced forward against pressure. Then, if m be the volume of the space through which any one of them moves during the expansion, the work done against the pressure it sustains is $p\ m$. The same reasoning applies to all the small portions into which the surface may be divided. Hence, by taking the sum of these quantities for the whole surface, it follows that the whole work done is $p\ v'$.

If the pressure vary, we may divide the increase of volume into parts so small that through each part the pressure may be considered constant, then for each the work done may be represented by the product $p\ v'$, and the work for the whole by $\Sigma\, p\ v'$, the sign Σ indicating that all the parts represented by $p\ v'$ are added together.

We may represent graphically as follows the work done by the expansion of a body against a pressure tending to resist the expansion :—

Let O A and O B represent the volumes of the body before and after expansion respectively, and let P Q be a line such that the ordinate at any point B represents the pressure corresponding to the volume O B. Let P A and Q B be the initial and final pressures. If the pressure be uniform, the figure A B Q P will be a rectangle; if the pressure be not uniform, P Q will be a curve, and in both cases the area A B P Q will represent the work done.

FIG. 3.



CHAPTER II.

THERMOMETRY.

The plan and object of this Chapter may be described as follows :—

(1.) Reference is first made to the familiar sensations experienced on touching in succession a number of bodies, some of which are warmer than others.

(2.) A scientific test, more delicate and trustworthy than that furnished by the sense of feeling, is established for distinguishing these differences.

(3.) The terms 'warmer' and 'colder,' which were associated with the sensations, are then replaced by the scientific phrases 'of higher and of lower temperature.'

(4.) Finally, a method is developed of definitely measuring differences of temperature.

§ 3. **Experiments. First Series.**—*Experiment I.*—It is a matter of common and every-day experience that when, in a room in which there is a fire, different objects at different distances from the fire are touched different sensations are produced, which lead us to say that some of the objects are warmer than others. If two portions A and B of the same substance, as, for instance, two pieces of the same metal, produce different sensations, described by saying that A is warmer than B, or, which is the same thing, that B is colder than A,

when they are placed in contact,—whether A be large or small compared with B,—A becomes colder and B becomes warmer, until no difference can be perceived.

If we take three bodies, A, B and C, such that there is no difference in the sensations of warmth or cold felt on touching A and C, or, which is the same thing, no change as regards warmth or cold when A and C are brought into contact, and similarly no change when B and C are brought into contact, then there is no change when A and B are brought into contact.

If we take three bodies A, B and C, such that A is warmer than B, and B warmer than C, then A is warmer than C; and if A is gradually cooled down until there is no change as regards warmth on connecting it with C, then, in this continuous change, A passes through a state which would not be changed if at that instant A were connected with B.

Experiment II.—When two bodies, A and B, of which A is the warmer, are brought into contact, the warming of B which follows is attended with some modification or change in the physical state of B. For instance, if A is a bath of boiling oil and B a rod of metal plunged into A, then a change of volume is produced in B. If B is a piece of ice, it is melted; if B is a piece of phosphorus it melts, ignites, and burns. If B is a vessel of water, the water boils.

Experiment III.—If a body, which changes its volume when heated, is placed at different times and under different circumstances in melting ice, under the normal pressure of the atmosphere, the volume is always found to be the same.

Such a body also always assumes the same volume whenever it is placed in the steam issuing from water boiling under a fixed pressure.

§ 4. **Discussion of the Experiments.**—The sensations referred to in Experiment I. are associated in our minds with the existence of the same power in different bodies. This power is termed HEAT. When two pieces of the same substance, *A* and *B*, of which *A* is warmer than *B*, are placed in contact, *A* acts towards *B* as a source of heat. *A* being warmer than *B*, heat passes from *A* to *B*, however small or however large *A* may be: so that the passage of heat is not determined by the *quantity* of heat in *A*, but by a quality of this heat, termed its *temperature*. When *A* is warmer than *B*, and therefore loses heat on contact with *B*, we say, in scientific language, that *A* has a higher temperature than *B*. If, when two bodies or two systems of bodies are placed in contact, no heat passes from one to the other, we say that their *temperatures are equal*, or that the two bodies or two systems are in *equilibrium as regards temperature*.

Whenever there is a passage of heat on connecting two bodies or two systems of bodies, we say that the two bodies or the two systems are initially at different temperatures; and that which acts towards the other as a source of heat, that is to say, which produces, in the other system, the effects,—such as expansion, fusion, or evaporation,—described in Experiment II., is said to have the *higher temperature*.

§ 5. **Definitions respecting Temperature.**—Premising that we may subsequently find reason for slightly modifying the definition, we may therefore

define the temperature of a body as the measure of its power to communicate heat to other bodies.

If, when two bodies are connected, there is no passage of heat from one to the other, the bodies are said to be in *thermal equilibrium.*

Bodies in thermal equilibrium are said to have equal temperatures.

When two bodies are placed in contact, that which loses heat is said to have the higher temperature.

When the temperatures of two bodies are equal to the temperature of a third body, the temperatures of the two bodies are equal to one another; or, two temperatures equal to a third temperature are equal to one another.

If, for example, A and B are two bodies, and C is a rod of metal, and if, when C is brought into contact with A, it experiences no change of volume, and if, when brought into contact with B, the volume of C again undergoes no change, then the bodies A and B are in thermal equilibrium, or have equal temperatures.

If, of three bodies, A, B and C, the temperature of B is lower than that of A, and the temperature of C lower than that of B, then is the temperature of C lower than that of A; and if C be brought to a source of heat so that its temperature is raised to that of A, then in passing from its original temperature it will assume all temperatures between those of C and A; and at one instant it will have a temperature equal to that of B, so that, if at that instant C were connected with B, there would be between them thermal equilibrium.

From this statement it follows that, when a number of bodies have different temperatures, they may be arranged in order, so that any one of them shall have

a higher temperature than all the bodies that precede it, and a lower temperature than all those that follow it.

Suppose a number of bodies, represented by the letters *A*, *B*, *C*, *D*, &c., to be so arranged, then it is evident that no other arrangement of the bodies will be equivalent to this one; that is to say, there is only one way in which they can be arranged in order of temperature.

When thus arranged, any one of the series of bodies, in passing from its initial temperature to that of any other of the series, must pass through the temperatures of all the intermediate bodies.

Temperature is therefore a quantity capable of continuous variation and therefore of measurement, provided we can establish a fixed temperature to measure from and a fixed unit of temperature.

Now Experiment III. shows that both the temperatures of melting ice and of boiling water are constant. The first may therefore serve for the fixed temperature, and the interval between them for a fixed unit of temperature.

We have yet, however, to determine how this constant interval of temperature may be subdivided into equal parts. To make the subdivision, a body is used which undergoes a continuous increase of volume when its temperature is raised continuously through the interval described above.

§ 6. **Measurement of Temperatures.**—Suppose a number of bodies, represented by the letters *A*, *B*, *C*, &c., to be arranged in order of temperature.

Let a rod of metal be heated until it has a temperature equal to that of the body *A*, and suppose its

length to be then measured; let the rod be then kept at a source of heat until it has a temperature equal to that of B, and let its length be again measured, and so on for the whole series of bodies. The rod will have a particular length for each temperature, and it will be sufficient to know this length for any one of the bodies, in order to determine the relation of its temperature to the temperatures of the other bodies. If for two of the bodies the rod has the same length, the temperature of these bodies will be equal. If for two others it has different lengths, that for which the length of the rod is the greater has the higher temperature. The rod when used for comparing temperatures would be called a 'thermometer.'

A thermometer is an instrument for measuring the temperatures of bodies.

We may take, as the measure of the temperature of a body, the length, the volume, or any function of the length of the thermometer. By this means temperature is represented by a number which satisfies two conditions :—

1. That two bodies are in thermal equilibrium for which this number is the same.

2. That two bodies for which the number has different values are not in thermal equilibrium, but, when they are placed in contact, that to which the higher number corresponds acts towards the other as a source of heat.

Instead, however, of taking the actual volume of the thermometer for the number representing the temperature, the following conventions are universally adopted :—

1. That temperature is called zero for which the thermometer takes a particular volume, v_0, arbitrarily chosen.

2. That temperature is called the number n at which the volume of the thermometer becomes v_0+n. The number n is positive or negative, according as the change of volume considered is an expansion or contraction.

3. The unit by which n is measured is usually a certain fraction of the increase of volume which the thermometer undergoes in passing from one temperature, determined by some physical phenomenon which may be easily reproduced with exactly the same conditions, to a second temperature similarly determined by some other phenomenon.

The two fixed temperatures most readily fulfilling this condition are :—

1. The temperature of melting ice.

2. The temperature of the steam which issues from water boiling under a pressure of 76 cm. of mercury, this mercury being at the temperature of melting ice.

Fahrenheit took for his unit of volume the 180th part of the increase of volume of his thermometer in passing from one of these temperatures to the other, and he took for *zero* that temperature at which the thermometer had a volume less by 32 of these units than the volume it had when placed in melting ice.

According to Fahrenheit's plan, therefore, the thermometer must be placed first in melting ice and the volume marked or measured. Secondly, it must be placed in steam, issuing from water boiling at the normal pressure, and the volume again noted.

The increase of volume is then represented by 180, and the volume of the thermometer at the temperature of melting ice is represented by v_0+32. Then, when the thermometer takes a volume v_0+n, the temperature is said to be n degrees Fahrenheit or $n°$ F. On this scale, therefore, the temperature of melting ice is 32 and that of boiling water 212.

Réaumur, after finding the change of volume between the two fixed temperatures, calls this change 80, and the volume at the temperature of melting ice v_0; as before, v_0+n being the volume of the thermometer, the temperature is said to be $n°$ R. On this scale, therefore, the temperature of melting ice is 0° and that of boiling water 80°.

In the Centigrade thermometer the change of volume between the two fixed temperatures is called 100, and the temperature of melting ice is called zero as in Réaumur's plan. If v_0 be the volume at 0°, the unit being the 100th part of the change of volume between the fixed temperatures, then when the volume of the thermometer is v_0+n the temperature is $n°$ C.

The degree Centigrade is therefore the rise of temperature of a thermometer which experiences a change of volume equal to the 100th part of the change which it would experience in passing from the temperature of melting ice to that of boiling water.

We have not yet, however, arrived at a sufficiently definite measure of temperature, for the question naturally suggests itself—is there any difference in the indications given by thermometers composed of different substances? If we make thermometers of different substances, and graduate them according to

the preceding method, so that they give the same numbers for the temperatures of melting ice and boiling water, experiment shows that they will not give the same measure for a given intermediate temperature.

If, for instance, there are two thermometers, containing respectively mercury and alcohol, and graduated independently of each other, when one receives half as great an increase of volume in passing from 0° to the given temperature as it receives in passing from 0° to 100°, the other will probably receive, between the same temperatures, rather more or less than half the increase of volume it undergoes between 0° and 100°. So long as we keep to the same liquid our thermometers, graduated in the way described above, agree amongst themselves, but the agreement disappears when we take different liquids. It is necessary, therefore, to know what is the substance composing the thermometer. Moreover it is desirable to discover, if possible, whether a substance exist by means of which we can determine equal intervals of temperature, and if not, what substance approaches nearest to correctness in this respect.

From practical reasons, mercury is most frequently adopted as the substance whose expansion measures changes of temperature.

There are, however, reasons, which will appear subsequently, for believing that measurements of temperature furnished by gas-thermometers are more correct than those given by liquids and solids. But it is found by experiment that the indications of a well-made mercury-thermometer do not differ from those of a

gas-thermometer by more than about half a degree, at any temperature between 0° and 100°, or by more than a few degrees at any temperature at which a mercurial thermometer can be used at all. Hence the indications of such a thermometer may be taken as sufficiently correct measures of temperature for many common purposes.

We will at present mention only two reasons for supposing that gas-thermometers are more accurate than thermometers made with solids or liquids: these are—

1. Thermometers, which measure temperature by the expansion of the permanent gases, although they differ from liquid thermometers, agree amongst themselves.

2. If equal quantities of heat are given to a permanent gas they cause equal increments of volume.

FIG. 4.

Dry air is the permanent gas most easily obtained, hence the gas-thermometer usually adopted is the air-thermometer.

The air in such a thermometer must be kept under the same pressure, or must be accompanied by a barometer, which will enable us to determine the pressure.

For instance, the thermometer may consist of a bulb and tube filled with dry air, and inverted with the open end of the tube in mercury (fig. 4). Then constancy of pressure will be secured by depressing or raising the tube in every experiment until the height of the barometer, less the difference of level between the mercury inside and outside the tube, has the same value.

CHAPTER III.

HEAT A MEASURABLE QUANTITY.

This Chapter treats of a branch of the Science of Heat termed Calorimetry, or the investigation of methods of measuring quantities of heat. We may indicate the argument of the Chapter as follows :—

(1.) Heat may pass from one body to another, so that the amount of heat in a body is capable of being increased or diminished. When it passes into a body it usually produces some change or changes in the body's physical state, and the quantity of change produced readily suggests itself as a measure of the quantity of heat.

(2.) Quantities of heat may be accurately compared without an evenly-divided scale of temperatures, so that the knowledge of quantities of heat may be used to test the scale of temperatures.

(3.) The experimental fact that different quantities of heat are required to raise equal masses of different substances through the same interval of temperature leads to the recognition of a property of bodies called *specific heat*, and to an enquiry into methods of measuring it.

(4.) Finally, we examine the circumstances under which heat may be given to a body without changing its temperature.

§ 7. **Experiments. Second Series.**—*Experiment I.* —Equal weights of water at the same temperature, in cooling down to 1°, will always raise the temperature of the same weight of water from zero to 1°.

The same remark applies to equal weights of the same substance, whatever it may be.

Experiment II.—When equal weights of different substances—as, for instance, a pound of water and a pound of mercury at the same temperature, above 0°—are placed in water at 0°, in cooling down to the temperature of 1°, they will raise the temperature of different quantities of water through the same temperature; as, for example, 1°.

And, generally, the quantity of heat needed to effect a given change of temperature is different for different substances.

Experiment III.—Let a thermometer be inserted in a vessel of ice; let a little hot water be poured into the ice and stirred. The thermometer will give the same indication as before, but some of the ice will melt. The experiment may be repeated again and again, as long as ice remains, showing that to melt ice heat must be given to it, and that this heat does not affect the temperature.

If 790 grammes of water at a temperature of 10° C. be mixed with 100 grammes of ice at 0° C., provided no heat enters or leaves the mixture, the result will be 890 grammes of water at 0°. Hence 79 grammes of water in cooling 1° C. give out heat which will melt 1 gramme of ice at 0° C., without changing the temperature.

Experiment IV.—Let steam from a boiler in which there is a thermometer pass into a vessel of cold water, also containing a thermometer. The steam will condense, and the temperature of the water will be raised. The condensation of steam will continue

until the water originally in the vessel and the water resulting from the condensation have the same temperature as the steam issuing from the boiler. Hence the steam in condensing gives out heat, without itself changing its temperature. For example, if the vessel contain 1,000 grammes of water at 47° C., when, in consequence of the condensation of steam, which enters it at the temperature of 100°, the temperature of the water in the vessel is raised to 100° C., it will be found that the weight of water in the vessel is 1,100 grammes. Thus 100 grammes of steam at 100° C., in condensing to water at 100° C., raises the temperature of 1,000 grammes of water through 53° C. Hence 1 gramme of steam would raise 10 grammes of water through 53° C., and therefore 1 gramme of water through 530° (more exactly 536°).

§ 8. **Discussion of the Experiments.**—Whenever heat passes from one body *A* to another *B*, so that the temperature of *A* falls, and some change, such as a rise of temperature or a change of state, results in *B*, then, if in repeated experiments the fall of temperature of *A* has the same limits, the change in *B* is always the same. And, generally, whenever a number of bodies, forming a system which, as a whole, neither loses nor gains heat from without, have initially different temperatures, there are always definite relations between the fall of temperature and change of state of the bodies that give out heat, and the rise of temperature or change of state which the other bodies of the system simultaneously experience.

We are naturally led, therefore, to regard heat as a measurable quantity, and to conclude that quantities

of heat may be expressed in terms of any of its directly measurable effects. To measure heat, a standard substance in a stated initial condition has to be chosen, and the effect of heat upon this substance has to be defined. The standard substance may, for example, be ice at the melting-point, and the effect of the heat, the melting of the ice without changing its temperature. The quantity of heat producing the effect will be measured by the mass or quantity of ice melted. The plan, however, which is most generally adopted is to select a particular kind of matter, and use the heat to be measured in raising the temperature from one given value to another; the quantity of matter in which the defined effect is produced is then the measure of the quantity of heat employed in producing it. The readiest unit of heat, according to this plan, is the amount of heat which will raise the temperature of a unit of mass of distilled water from *zero* to 1°.

If the temperature of a body falls, or the state of a body changes in such a way that the whole of the heat which the body loses during the change is employed in raising the temperature of m units of mass of water from zero to 1°, then we say that the body gives out and the water receives m units of heat.

Heat of all kinds, whatever be its source, can be measured in the same way; and quantities which are represented by the same number, because they produce the same amount of change in the standard substance, are regarded as equivalent, whatever the source from which the heat comes. This leads us to what must be regarded as the fundamental principle on which the measurement of quantities of heat depends.

§ 9. **Carnot's Axiom.**—If a body, after having experienced any number of transformations, be brought identically to its primitive physical state as to density, temperature, and molecular constitution, it must contain the same quantity of heat as that which it initially possessed; and if any body in a given state is first heated so as to pass through a series of states, and then allowed to cool to the original temperature, *passing while cooling through exactly the same series of states in reverse order*, the quantities of heat lost by the body during one set of operations are precisely compensated by those which are absorbed by it during the other set.

The words in italics are added to Carnot's statement of this axiom; and, as we shall show in a subsequent Chapter, the statement would not in general be true without them. When a body passes through a series of changes, at the end of which it is in precisely the same state as at the beginning, although the quantity of heat in it at the beginning and at the end of the series of changes is the same, the heat absorbed and the heat given out may be different, unless the series of changes in the departure from the initial state be identical, though in inverse order, with the series of changes in the return to the initial state.

For example, we may raise the temperature of cold water to 100° and then convert it into steam at this temperature; the steam thus produced may escape into the air, and be cooled by the air to its own temperature, without being condensed until it comes in contact with a surface colder than the air, when it will be deposited as dew. Taking as the

extreme conditions cold water and steam, it is evident that in passing from one of them to the other the water does not go through the same series of states as it does in returning, and accordingly it cannot be affirmed that the heat given out in the second part of the change will be equal to that taken in during the first.

§ 10. **Definition of Specific Heat.**—If a unit of mass of a substance absorbs a quantity of heat q in passing from a temperature T to a temperature $T+t$, then the ratio $\frac{q}{t}$ is termed the *mean specific heat for* $t°$ (t degrees) *from the temperature* T.

The limit of the ratio $\frac{q}{t}$, as t is diminished, is termed the *true specific heat at the temperature* T.

Generally the mean specific heat varies so slowly, that for a small range of temperature—as, for example, 1°—it may be regarded as sensibly constant, so that generally the mean specific heat for 1° and the true specific heat are regarded as equal.

The specific heat of a body for which this holds good may, therefore, be defined as the ratio of the quantity of heat required to raise that body through a small range of temperature—as, for instance, 1°—to the quantity required to raise an equal weight of water, initially at 0° C., through the same range of temperature; or, which is the same thing—If the quantity of heat required to raise the temperature of 1 gramme of water from 0° C. to 1° C. be taken as unity, then the quantity of heat required to raise the temperature of 1 gramme of a given substance 1° is,

without appreciable error, the specific heat of the substance.

Use of the comparison of quantities of heat to test the accuracy of the thermometric scale.

We have mentioned two ways of comparing quantities of heat.

1. Two quantities of heat are to one another as the masses of ice at 0° C., which they will severally melt without changing the temperature.

2. Two quantities of heat are to one another as the masses of a standard substance, which they will severally raise through the same interval of temperature.

Now, when the first method is employed, the melting of the ice takes place at a constant temperature; and, to use the second method, we have simply to find the masses of a standard substance which the quantities of heat to be measured will raise through identically the same interval of temperature. Hence, even with a defective thermometric scale, we may arrive at definite and accurate measures of quantities of heat. We may therefore use these methods to test the accuracy of the thermometric scale.

The first question to be asked is—Are two quantities of heat equal, if they raise the temperatures of equal masses of any substance, or of a particular substance chosen as a standard, through the same number of degrees not in the same part of the thermometric scale? If, for instance, the temperature of a gramme of water be raised from 0° C. to 10° C. and that of another gramme of water from 10° C. to 20° C., will the quantities of heat absorbed be the same?

It has already been stated that if an air- or gas-thermometer be graduated in the way described in Chapter I., equal quantities of heat given to it in succession cause equal increments of volume, but this is not generally the case with solids, liquids, and condensable gases.

We assume for the present, therefore, that the air-thermometer is that which accurately subdivides the interval between the temperature of melting ice and the temperature of boiling water. Since the degrees of temperature on an air-thermometer are equal intervals of temperature, and equal quantities of heat raise the temperature of the same mass of air kept at constant pressure through the same number of degrees, it follows that the specific heat of air under constant pressure must be constant.

We shall henceforth suppose any mercurial or other thermometer used in experiments, or referred to in the illustrations and theorems, to be graduated by comparison with an air-thermometer, so that the degrees upon it represent equal intervals of temperature.

The specific heat of water is found to rise with the temperature, but so slowly that we may assume it constant for several degrees without appreciable error. For example, from 0° C. to 50° C. it increases by about four-thousandths of its value at the lower temperature. If the specific heat of water at 0° C. be unity, that at 50° C. is 1·004 and that at 100° C. 1·013.

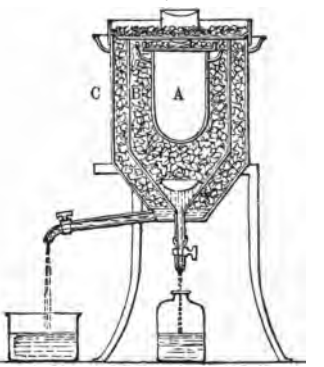
§ 11. **Methods of determining Specific Heats.** —Three methods have been employed to measure

the amount of heat given out by a body on cooling, or taken in while the temperature rises through a given number of degrees.

(1.) *The Method of Melting Ice.*—It is evident from the definition that the quantities of ice melted by equal masses of two bodies in cooling from the same temperature to that of melting ice, provided all the heat is used in the melting, are to one another as the specific heats of the bodies. Hence one way of finding the specific heats of bodies by experiment is to arrange a vessel of ice at the melting point, so that when a warm body is placed in the ice all the heat given out during the cooling of the body will be used in melting the ice, and so that the quantity of water produced can be determined. There are two methods commonly adopted for securing these conditions.

(*a.*) *The Calorimeter of Laplace and Lavoisier.* — This consists of three vessels, A, B and C, one fitting within another (fig. 5).

FIG. 5.



A, the inner vessel, is made of thin sheet copper or fine copper gauze, and is intended to receive the body which is to give out the heat to be measured.

B entirely surrounds the first, and contains the ice which the heat from A is to melt. The water

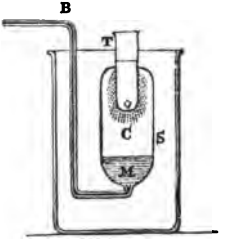
produced by the melting flows through a tube into the beaker set to catch it.

C entirely surrounds the second vessel and is filled with broken ice. Its purpose is to prevent heat from the outside from passing to B. The water from C runs off to a vessel distinct from that which receives the water from B.

There is a source of error in the estimation of the amount of ice melted in this instrument, which it is not easy to eliminate. Water will always adhere to the ice in the vessel B, and as during the experiment the position, shape, and amount of surface of the ice are changed, it cannot be assumed that the amount of water adhering to the ice is the same at the end as at the beginning.

(*b.*) *Bunsen's Calorimeter.*—This calorimeter is a vessel containing ice and water, with a means of determining any change in the volume occupied by them. As water occupies less space than the ice from which it is formed, the quantity of ice melted can be calculated from the change of volume which the mixture undergoes. The figure represents the instrument; T represents a test-tube of thin material, containing water at 0° C., into which the small heated body to be tested is dropped. As water a little above 0° C. is denser than water at 0° C. the warmed water will not rise, but remaining at the bottom of the test-tube will give its heat by conduction through the substance of

FIG. 6.



the test-tube to the ice and water outside. C is the calorimeter, containing ice and water above and a little mercury below, which also occupies part of the tube B. Any change in the volume occupied by the contents of C will be shown by the motion of the extremity of the mercury in the tube B.

§ 12. **Proposition.**—2. *Method of Mixtures.*—A thin brass vessel with polished surface contains water at a temperature t_1, and a body of mass m is quickly removed from a vessel, the temperature of which is t_2, and immersed in the water, and the whole assumes a temperature t. Having given the mass w of the water, the mass a of the vessel, and s its specific heat, and supposing that no heat leaves the vessel, find the specific heat x of the body.

Equate the sum of the units of heat possessed by the three masses before and after the experiment, beyond the heat which they would possess if they were at the temperature 0°.

The vessel has firstly $a\,s\,t_1$, and secondly $a\,s\,t$.

„ water „ $w\,t_1$, „ „ $w\,t$.

„ body „ $m\,x\,t_2$, „ „ $m\,x\,t$.

Hence $a\,s\,t_1 + w\,t_1 + m\,x\,t_2 = a\,s\,t + w\,t + m\,x\,t$.

From which equation x can be determined. We may take account of the heat absorbed by the glass and the mercury of the thermometer, and by the apparatus for stirring, by introducing on the first and second sides of the equation respectively the product of the mass, specific heat, and temperature before and after the experiment, for each.

We may correct the formula for loss of heat by radiation and conduction by adding to the second side of the equation a term R, the value of which may be determined by methods to be subsequently described.

This method of determining the specific heats may be used not only for solids but, by using thin glass vessels, for liquids also.

Description of Regnault's Apparatus for applying the Method of Mixtures.

This apparatus consists of two parts—the heating apparatus and the calorimeter.

The heating apparatus comprises (A) the boiler, (B) a steam jacket, with three concentric compartments; the inner one for receiving the body to be heated, the middle one supplied with steam from the boiler, and the outer one, a steam chamber to prevent cooling by contact with the outside air. (C) a wire cage in which the body to be experimented on can be first lowered into the middle of the *steam* jacket, and when it has acquired the temperature of the steam dropped carefully into the calorimeter.

The calorimeter is frequently made to run on wheels, that it may be easily moved to a place in which it is protected from draughts and radiation.

(3.) *Method of Cooling. Principle of the Method.*—Let t be the difference between the temperature of a system of bodies and the surrounding medium.

Let M_1 be the sum of the masses of the different bodies of the system, multiplied by their respective specific heats; and let t' be the very small variation of the temperature of the system which takes place in a very short time x'_1.

The loss of heat in this short time is evidently

$$M_1 . t'.$$

But this loss of heat depends only on the temperatures of the system and of the bodies which surround it, or the room in which the system is placed. Since the time x'_1 is very short, the loss of heat may be represented by the product of x'_1 into some quantity F, which we know depends only on the temperatures of the system and of the surrounding things, but the form of which it is not necessary to determine.

$$\therefore M_1 . t' = F . x'_1.$$

Let us now take another system, in which the sum of the products of the masses by their specific heats is M_2. Let the *second* system be enclosed in the same chamber, or have identically the same surroundings as the *first*, and let it be initially at the temperature t above the surrounding medium; then if x'_2 be the very short time required by the system to cool through the small variation of temperature t', we have:

$$M_2 . t' = F . x'_2.$$

From these two equations it follows that

$$\frac{x'_1}{M_1} = \frac{x'_2}{M_2}$$

Let the whole temperature t be divided into small parts t', then similar equations hold for each of the small portions of time, into which the time of cooling may be divided, and, by addition

$$\therefore \frac{\Sigma x'_1}{M} = \frac{\Sigma x'_2}{M_2}$$

or the quantities M_1, M_2 are to one another as the times of cooling of the two systems between the same limits of temperature.

If the masses of the bodies are equal, then M_1 and M_2 are to one another as the specific heats of the bodies; and in this case, therefore, the times of cooling are as the specific heats. If in addition one of the bodies is distilled water, the specific heat of which is unity, then the ratio of the times of cooling of equal masses between the same temperatures is the specific heat of the other body.

Description of Apparatus used by Mayer.—The cooling chamber used by Mayer and also by Regnault is a metal receiver, from which the air can be drawn by an air-pump; this receiver is placed in a bath of water at a known and constant temperature, or in a bath of broken ice. The inside of the receiver is coated with lampblack. In the middle of it hangs a small cage of silver, polished on the outside, and containing the body to be experimented on. The chamber is also supplied with a thermometer.

If the time of cooling of a given liquid between two temperatures be divided by the time of cooling of an equal mass of distilled water between the same temperatures, the result will be the specific heat of the given liquid.

This method is not suitable for solids, but is particularly useful for investigating the variation with change of temperature of the specific heat of any given liquid.

§ 13. **Definition of Latent Heat.**—The latent heat of a substance is the quantity of heat which must be

given to a unit of mass of the substance in a given state in order to convert it into another state without changing its temperature.

There are for most substances two changes of state, namely, the change from the solid to the liquid, and the change from the liquid to the gaseous state. Hence for such substances there is a latent heat of liquefaction and a latent heat of vaporisation.

Heat may also, under certain conditions, be given to a gas without changing its temperature; and this fact leads to the recognition of a third kind of latent heat, which will be discussed in a subsequent chapter, when we consider especially the properties of gases.

It will be at once seen from the definition that the method of mixtures affords a ready means of determining latent heats. Experiments III. and IV. show that when we use the centigrade thermometer the latent heat of liquefaction for water is 79 at 0°, and the latent heat of vaporisation 536 at 100°. If we use degrees Fahrenheit, these numbers are replaced by 143 and 965.

§ 14. **Proposition.**—A quantity of water of mass m_1 and temperature t, in cooling to 0°, is found to melt a mass of ice m_2; supposing the mean specific heat of the water between 0° and t° to be unity, find the latent heat of liquefaction for water.

Let x be the latent heat required—that is, let x be the number of units of heat which a unit of mass of ice at 0° absorbs in becoming water at the temperature of 0°.

Then $x m_2$ = the heat absorbed by the ice,

$t m_1$ = the heat given out by the water.

$$\therefore x m_2 = t m_1$$

$$\therefore x = \frac{t m_1}{m_2}.$$

§ 15. **Proposition.**—A body of mass m_1 and temperature t is placed in ice at the melting-point, and is found to melt a mass m_2 of ice: to find the specific heat of the body.

Let l be the latent heat of liquefaction; that is to say, the number of units of heat which a unit of mass of ice absorbs in becoming water at the same temperature.

Let x be the mean specific heat of the body between 0° and t°.

The quantity of heat given out by the body is

$$m_1 x t,$$

and the heat absorbed by the melted ice is

$$m_2 l.$$

Therefore, if no heat escapes by conduction or radiation,

$$m_1 x t = m_2 l$$

$$\therefore x = \frac{m_2 l}{m_1 t}$$

CHAPTER IV.

VAPORISATION.

It will be convenient to discuss in this Chapter the laws according to which vapours are formed in enclosed spaces:—

(1.) When their liquids are introduced into vacua;

(2.) When they are introduced into spaces already occupied by a gas.

We then have to show how to determine by experiment the pressures exerted by vapours at any given temperature.

§ 16. **Experiments. Third Series.**—*Experiment I.* Take a series of barometer-tubes, *a*, *b*, *c*, *d*, &c., of the same size, 36 inches long, fill them, and invert them in the same cistern of mercury, as in the figure. The mercury will, of course, stand at the same level in all the tubes, and there will be a vacuum at the top of each.

Now, without altering the tube *a*, carefully insert into *b*, *c*, *d*, &c., by means of a pipette, different liquids—as, for instance, water, alcohol, ether. In every case, whatever the temperature, a depression of the mercurial column will be observed, showing that a fluid has been formed in the space above the

mercury, capable of exerting an elastic force in the same way as a gas. By introducing sufficient liquid into each tube, we may cause an excess of liquid to remain, so that the same substance exists at the same time in the liquid and gaseous state in the space above the mercurial column.

FIG. 7. *d c b a*

The elastic force or pressure of the vapour in any tube may be ascertained by noting the difference of levels of the mercury in this tube and in the tube *a*. If, for example, the mercury in *a* stands at the height of 30 inches, and in another tube *b* at 27 inches, then we say that the pressure exerted by the vapour in *b* is equal to that exerted by 3 inches of mercury.

In making and varying the experiment the following facts appear :—

(*a.*) The pressures exerted by different vapours at the same temperature are different, and depend only on the nature of the liquids from which they are formed.

(*b.*) If the tubes *b*, *c*, and *d* are placed in a deep cistern, and pushed down into the mercury, the pressure of each vapour remains the same, although the space above the mercury is diminished : hence some of the vapour condenses again into liquid. We see, therefore, that the elastic force of a vapour, which is in contact with its own liquid at a given temperature, is independent of the space occupied. If we increase the space so that the excess of liquid is completely vaporised, the pressure or, as it is often called, the

tension varies nearly in the inverse ratio of the volume, and the vapour therefore resembles a gas.

(*c.*) If the liquid is introduced into a space containing a gas instead of into a vacuum, the vapour exerts for a given temperature and volume the same pressure as in a vacuum.

For example, if when the mercury in *a* stands at 29 inches, water introduced into *b* depresses the mercury to 26 inches, then if we put sufficient dry air into a third tube *c* to depress the column to 20 inches, on introducing water the column will descend to 17 inches. That is, whether air is present or not in the space occupied by the vapour, the tension of the vapour is equal to the pressure of 3 inches of mercury.

(*d.*) If the tubes are surrounded with a water-bath, and the temperature is continuously raised, the pressures of the vapours increase with the temperature; and when the temperature of the water-bath reaches the boiling-point of any of the liquids, the mercury in the tube containing that liquid is driven down to the level of the mercury in the cistern, thus showing that, at the boiling-point of a given liquid, the tension of its vapour equals the atmospheric pressure.

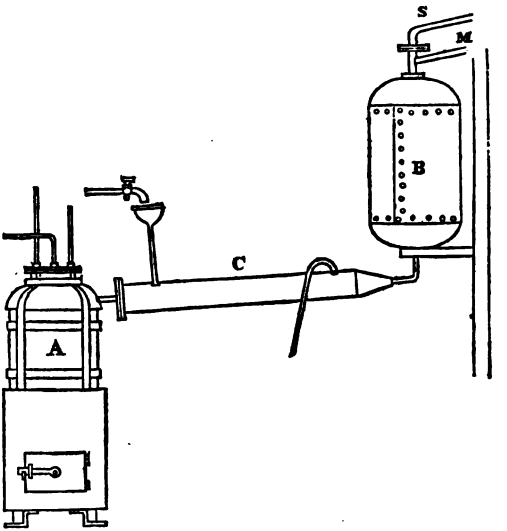
Experiment II.—If a vessel of hot water, having a temperature below the ordinary boiling-point—as, for instance, 70° C.—is placed under the receiver of an air-pump, and the receiver rapidly exhausted, the water is seen to boil violently, showing that when the pressure is diminished the boiling-point is lowered.

If water is heated in a Papin's Digester, that is to say, in a closed boiler containing thermometers, and supplied with a safety-valve, kept down by a lever and

movable weight, it is found that the temperature at which the water boils can be raised at will by increasing the pressure on the valve.

§ 17. **Discussion of the Experiments.**—These experiments suggest two methods of determining the

FIG. 8.



pressure of a vapour in contact with its own liquid at a given temperature.

1. If the temperature is below the ordinary boiling-point of the liquid, we introduce the liquid into the vacuum of a barometer-tube, and observe the fall of the column of mercury.

2. If the temperature is above that of the ordinary

boiling-point of the liquid, we cause the liquid to boil in a vessel in which there are thermometers, and connected with an apparatus enabling us to increase at will the pressure of the atmosphere on the surface of the liquid, and at the same time to measure this pressure. The pressure under which the liquid boils at any temperature is the maximum tension of the vapour at that temperature.

The apparatus, as used first by Dalton, and afterwards by Regnault, is shown in fig. 8.

It consists of:

(*a.*) A boiler, A, through the top of which several delicate thermometers are fitted. This contains the liquid.

(*b.*) An air-vessel, B, connected on one side with the boiler, and on the other side by a tube M, with a manometer for measuring the pressure of the air. The air-vessel has a supply-tube and stop-cock S, so that air can be forced into it to any given pressure.

(*c.*) A cold-water condenser, C, surrounding the tube which connects the air-vessel with the boiler. This tube inclines towards the boiler, so that the vapour, which rises in consequence of the ebullition, may be condensed in the tube, and flow back to the boiler.

The boiling of the water may be recognised by the sound produced, and by the steadiness of the indications of the thermometer, and the pressure under which the ebullition occurs is shown by the manometer.

CHAPTER V.

EXPANSION.

The treatment of the expansion of bodies by heat naturally divides itself into three parts, each of which presents an experimental problem. For example:

(1.) Since solids expand by a small fraction of their volumes, it is necessary to devise means of magnifying the expansion in order to measure it.

(2.) When liquids expand, the vessels containing them also expand at the same time, and a method has to be found of separating the two expansions.

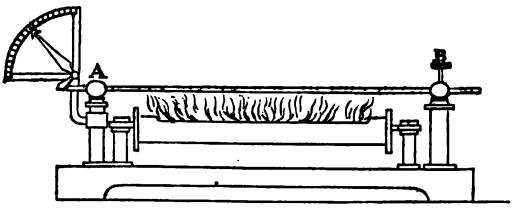
(3.) The expansion of a gas depends not only on the change of temperature but also on change of pressure, and a definite relation is found to exist between the pressure, temperature, and volume of a gas, which may be represented either by an algebraical formula or geometrically.

§ 18. **Experiments. Fourth Series.** *Experiment I.*—(*a.*) A rod of metal, when one end is placed against a fixed support, B, and the other is placed against a movable index, A, is found to increase in length as the temperature is raised (fig. 9).

(*b.*) A globe of metal, which at a low temperature will just pass through a ring of metal, after having been immersed in hot water, or heated in the flame of a lamp, will not pass through the ring (fig. 10). This shows that the expansion is not in one dimension only

but is an increase of volume, and in the case of a homogeneous solid the expansions in any two directions are proportional to the lengths in these directions.

FIG. 9.



(*c.*) If a flask be filled with a liquid and fitted with a tube, as in fig. 11, the expansion of the liquid

FIG. 10.

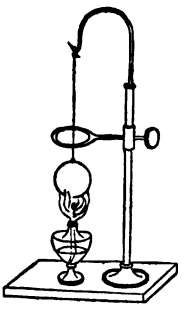
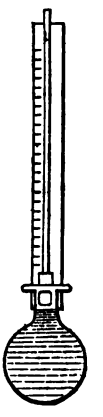


FIG. 11.



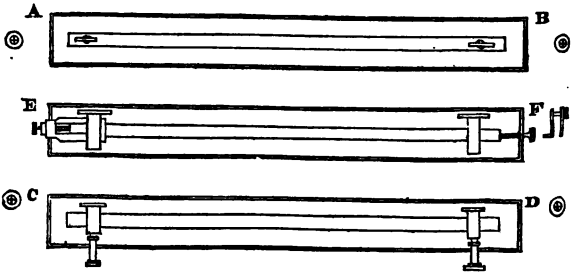
with rise of temperature is seen to be more rapid than that of the solid glass.

(*d*.) If the flask contain a gas the expansion is still more rapid.

Experiment II.—Ramsden's Method of measuring the expansion of a metal bar.

The apparatus consists of three equal and parallel troughs, in the middle one of which the bar, E F, to be tested is placed, and in the others two iron bars, A B and C D, kept at a constant temperature by being

FIG. 12.



surrounded with ice. To the two ends of the iron bar contained in the trough, C D, there are fixed two lenses, serving as eye-pieces of small telescopes, with crossed vertical and horizontal threads in the field of view, and on the extremities of the bar, E F, in the middle trough are placed two other lenses, serving as object-glasses to the former. On the ends of the last bar, A B, are crossed threads, illuminated by help of a small mirror, serving as objects to be looked at through the telescopes formed by the lenses. The bars are permanently fixed at one end, and movable through a collar at the other. Hence the eye-pieces

on the first bar, the two marks on the third bar, and one object-glass, namely, that on the right of the middle bar, may be regarded as rigidly fixed, inasmuch as there is no expansion or contraction of the two outer bars through change of temperature. But the left hand extremity of the middle bar, and consequently the object-glass attached to it, is movable, and will move towards the left when the bar expands. On the right side, therefore, the eye-piece, object-glass, and mark are fixed, and on the left the eye-piece and mark are fixed, but the object-glass is movable. The vertical thread in the left hand eye-piece at the beginning of the experiment, when all the three troughs are filled with melting ice, is made to lie before and hide the vertical thread in the left-hand mark. But when the ice of the middle trough is replaced by hot water, so that the object-glass of this telescope has been moved owing to the expansion of the middle bar, this thread will no longer seem to coincide with the thread of the mark.

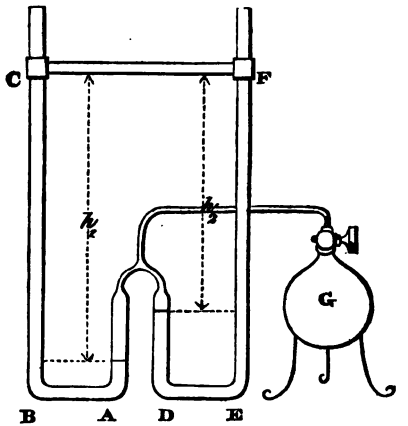
The coincidence of the thread may, however, be restored by means of a screw attached to the left object-glass on E F. The number of turns and fractional parts of a turn of this screw, necessary to make the thread of the telescope coincide with the thread of the mark, affords the means of calculating the expansion of the middle bar with very great precision.

Experiment III.—To determine the absolute expansion of Mercury. (Dulong and Petit, with modifications by Regnault.)

A B C and D E F (fig. 13) are two equal bent tubes,

having long arms, B C and E F, on the outsides respectively, and short arms at A and D towards the middle. The two arms in each are connected by the horizontal portions, A B and D E. The upper extremities of the long arms are connected by a tube, C F, and the upper extremities of the short arms communicate with the

FIG. 13.



same gas-holder G, which contains air at a pressure sufficient to support a column of mercury equal to B C or E F in addition to the pressure of the atmosphere. The arms, B C and E F, are surrounded with oil- or water-baths at different temperatures.

The mercury in the two longer arms has the same level at the top, difference of level being adjusted by the cross tube, C F, but the mercury in the short arms at A and D has not the same level. Hence the

heights, h_1, h_2, of the columns at different temperatures, t_1 and t_2, supported by the pressure of the gas in G, are different.

It will be proved subsequently (in § 23) that if a be the coefficient of absolute expansion per degree between t_1 and t_2, a is determined from the equation,—

$$\frac{h_1 - h_2}{h_1} = \frac{a\,(t_2 - t_1)}{1 + a t_1}.$$

All the quantities except a in the equation can be determined by observation during the experiment, and then a can be calculated from the equation.

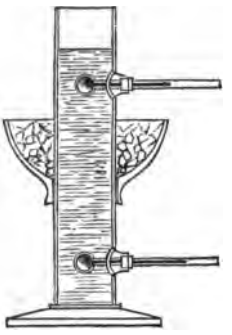
Experiment IV.—To prove that water has an anomalous expansion and a temperature of maximum density.

If a large flask, containing water at the ordinary temperature of the atmosphere, be fitted with a tube of small bore and a scale, as in fig. 11, and the whole immersed in a freezing mixture, such as a mixture of salt and pounded ice, the column in the tube descends; thus showing that the water at first contracts. But before the water in the flask begins to freeze this contraction stops, and the motion of the column is reversed; thus showing that water does not contract on being cooled below a certain temperature, and that there is a temperature of maximum density. On removing the flask from the freezing mixture the process is reversed; at first the liquid contracts as it gets warmer, and then expands.

(*b.*) Let us take a glass cylinder filled with water, at about the ordinary temperature, fitted with two thermometers, one near the top and the other near

the bottom, as represented in fig. 14. Let the middle of the cylinder be surrounded by an envelope filled with a freezing mixture. The temperature will immediately begin to fall, but the lower thermometer will at first change more rapidly than the upper one. This will continue until a temperature of about 4° C. is reached, when the indication of the lower thermometer remains stationary for some time. On the other hand, at the temperature of 4° the upper thermometer begins to fall more rapidly, and continues doing so until it reaches the freezing point, so that the indication of the upper thermometer overtakes that of the lower one and finally passes it. Although, during the first part of the experiment, the water at the top was warmer than that at the bottom, at the end, the water begins to freeze at the top, the water there being colder than at the bottom. The explanation is as follows. Water has a maximum density at about 4°, above which it contracts, but below which it expands as it cools. At first, therefore, the particles of water near the freezing mixture becoming denser descend, and are replaced by warmer particles from beneath, and this process stops when the temperature of the water at the bottom is reduced to 4°; below this temperature the colder particles are the lighter and in consequence ascend.

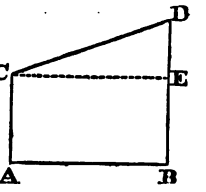
FIG. 14.



§ 19. **Remarks on the Experiments.**—*Mean coefficient of Expansion.*—Take a line, A B, on which to set off temperatures.

Let A represent the zero of temperature. Let lines perpendicular to A B represent volumes. Let A C represent the unit of volume at 0°, and B D the volume which this will attain at a certain temperature, $t°$; then $\frac{D E}{A B}$ is the mean coefficient of expansion from 0° to $t°$.

FIG. 15.



If the unit of volume of a substance at 0° be heated so that the temperature rises through $t°$, and the increase of volume be divided by t, the quotient is termed the mean coefficient of expansion between the limits of temperature.

Let a be the mean coefficient of expansion from 0° to $t°$. Then, if x be the increase of volume of the unit,

$$a = \frac{x}{t}, \text{ or } x = a\,t.$$

Hence that which is the unit of volume at 0° becomes $(1+at)$ when heated to $t°$.

If we take a body, therefore, which has V_0 units of volume at 0°, the volume at $t°$ will be

$$V_0\ (1+at).$$

Hence if V_1 and V_2 be the volumes at temperatures t_1 and t_2 of a substance which contains V_0 units of

volume at 0°, then, supposing we may regard a as constant up to the highest of these temperatures,

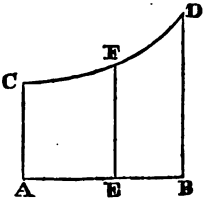
$$V_1 = V_0(1 + a\,t)$$
$$V_2 = V_0(1 + a\,t_2)$$
$$\therefore \frac{V_1}{1 + a\,t_1} = \frac{V_2}{1 + a\,t_2}. \quad . \quad . \quad \alpha$$

If D_1 and D_2 be the densities at the two temperatures, since the densities are inversely as the volumes,

$$D_1\,(1 + a\,t_1) = D_2\,(1 + a\,t_2) \quad . \quad . \quad \beta$$

True coefficient of Expansion.—Let A B be the line of temperature as before, and let lines perpendicular to A B represent volumes. Let A C represent the unit of volume of a substance at 0°, and let the ordinate E F at any point E represent the volume at the temperature represented by A E.

FIG. 16.



If the mean coefficient of expansion for A B be the same as the mean coefficient for A E, then C F D will be a straight line. But experiments show that this is not generally the case, and that the line C F D is a curved line, and that there are different coefficients for different parts.

Definition.—If that quantity of a substance which occupies a unit of volume at 0° be heated from a given temperature to a temperature very slightly higher, the limiting value of the quotient, obtained by dividing the small change of volume by the small change of temperature which causes it, is termed the true coefficient of expansion at the given temperature.

It is evident that the true coefficient of expansion at any temperature is the tangent of the inclination of the curve, C D, to the axis, A B, at the point corresponding to that temperature.

§ 20. **Remarks applying specially to the Expansion of Solids.**—The principal laws and facts proved by experiments on the expansion of solids are:

1. As a general rule solids expand when heated, but recover their original volume when they are restored to their original temperature.

2. There are a few exceptions to the general rule; for instance, it is said that for Rose's fusible metal there is a temperature (59° C.) at which expansion ceases, and if the temperature be increased beyond this point the metal contracts. Fizeau observed that iodide of silver contracts by heat and expands by cold, the phenomenon being perfectly regular and continuous between 10° and 70° C.

Again, a piece of vulcanised india-rubber, which is stretched by a weight to double its length, is shortened by a tenth when its temperature is raised 50° C., and the shortening effect increases rapidly with the stretching weight employed.

3. With regard to the recovery by a solid of its original volume when it resumes its original temperature, it is found that if a solid be cooled suddenly, in most cases its particles do not at once bring themselves into the condition which usually exists at the reduced temperature, and in consequence the substance is in a state of constraint, which continues often for a very long time. This is probably one

cause of the change of zero in a mercurial thermometer.

4. A homogeneous solid devoid of crystalline or organic structure expands in such a manner that its figure at one temperature is similar to that at another. From this fact, demonstrated by experience, it follows that the coefficient of cubical expansion of a substance is three times the coefficient of linear expansion. For let a represent the coefficient of linear expansion for a rise of 1° C. above 0°; also let l represent the length, and v the volume, of the substance at 0°: then the length at 1° will be $l(1+a)$. Since the volumes at 0° and 1° are similar, they are to one another as the cubes of their lengths, that is,

$$\text{as } l^3 : l^3(1+a)^3, \text{ or as } 1 : (1+a)^3.$$

Hence the volume at 1° will be

$$v(1+a)^3, \text{ or } v(1+3a+3a^2+a^3).$$

Now, since a is a very small fraction, the last two terms of the expression may be neglected. Hence the new volume is $v(1+3a)$, and therefore the coefficient of cubical expansion is $3a$, or three times the coefficient of linear expansion.

5. As an almost universal rule, the mean coefficient of expansion increases with the temperature.

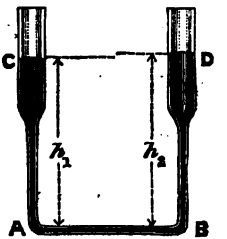
§ 21. **Remarks applying specially to the Expansion of Liquids.**—When experiments are made with the view of determining the coefficient of expansion of a liquid, the simultaneous expansion of the vessel presents a difficulty. The solid vessel which contains

the liquid must be heated with the liquid, and the expansion observed is really the resultant effect of the two independent expansions.

A method of determining the absolute expansion of a liquid, that is, the expansion independently of that of the envelope, is afforded by the following proposition, due to Boyle :—

§ 22. **Proposition.**—If the pressures of two vertical columns of the same liquid at different temperatures are in equilibrium with the same pressure, the heights of the columns are inversely as the densities.

FIG. 17.



Let h_1 be the height, and D_1 the density of the column, A C, at temperature t_1, and let h_2 and D_2 be the corresponding quantities for the column B D, having a different temperature t_2. Suppose the columns to communicate by the horizontal tube, A B, between the bases A and B. By hydrostatics, the intensity of pressure is $h_1 D_1$ at A, and $h_2 D_2$ at B, but, as there is no flow along A B, these pressures are equal—

$$\therefore h_1 D_1 = h_2 D_2.$$

§ 23. **Proposition.**—If the pressures of two vertical columns of the same liquid at different temperatures are in equilibrium with the same pressure, the difference of the heights is to the smaller height as the

expansion between the two temperatures is to the volume at the lower temperature.

Let us use the same letters as in the last proposition.

By that proposition we have—

$$h_1 D_1 = h_2 D_2,$$

and by equation β, § 19, if a be the mean coefficient of expansion between the temperatures 0 and t_2,

$$D_1(1 + a t_1) = D_2(1 + a t_2),$$

$$\therefore \frac{h_2}{h_1} = \frac{1 + a t_2}{1 + a t_1},$$

or, subtracting unity from both sides,

$$\frac{h_2 - h_1}{h_1} = \frac{a(t_2 - t_1)}{1 + a t_1}.$$

Here $1 + a t_1$ is the volume at $t_1°$ of that amount of liquid which has a unit of volume at 0°, and $a(t_2 - t_1)$ is the total expansion of this quantity of liquid between t_1 and t_2. Hence the proposition is proved.

Suppose t_1 to be zero.

$$\therefore \frac{h_2 - h_1}{h_1} = a t.$$

Hence, the absolute expansion of a unit of volume taken at 0°, when heated to any temperature, is equal to the difference of the heights of the two balanced columns at the two temperatures respectively divided by the height of the lower.

§ 24. **Proposition.**—The coefficient of absolute

expansion of a liquid is equal to its coefficient of apparent expansion in a vessel of any material, together with the coefficient of cubical expansion of the material of which the vessel is made.

Let a = the coefficient of absolute expansion of the liquid.

d = the coefficient of apparent expansion of the liquid.

c = the coefficient of cubical expansion of the material forming the vessel.

V = the volume of the liquid at 0°;
= also the volume of the portion of the vessel filled at 0°.

V' = the volume at 0° of the portion of the vessel filled by the liquid at 1°.

The real volume of the liquid at 1° will be

$$V(1+a).$$

The real volume of the portion of the vessel occupied by it will be $V'(1+c)$.

$$\therefore V'(1+c) = V(1+a).$$

$$\therefore \frac{V'-V}{V} = \frac{a-c}{1+c}.$$

But the first of these terms, being the ratio of the apparent increase of volume to the volume at 0°, is the coefficient of apparent expansion of the liquid.

$$\therefore d = \frac{a-c}{1+c}$$

$$\text{or, } d + dc = a - c.$$

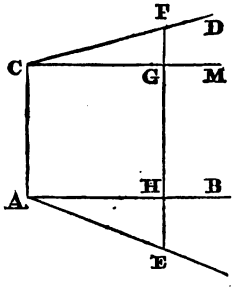
But as d and c are both small quantities, the term $d\,c$ may be neglected.

$$\therefore\ a = d + c.$$

This may be represented graphically thus :

Let A C represent the unit of volume, and let temperatures be set off along A B or C M, the point A or the point C representing 0°. Let G E represent the volume which A C would become at a temperature C G, the material being that of the vessel, and let H F be the volume which A C would appear to become when the material is the liquid contained in the vessel.

FIG. 18.



Then E F represents the volume which the liquid really occupies at the latter temperature. Now let A H represent 1°.

Then E F − A C = a, the coefficient of absolute expansion.

H F − A C = d, the coefficient of apparent expansion.

G E − A C = c, the coefficient of cubical expansion of vessel, and evidently $a = d + c$.

§ 25. **Proposition.**—Having given the absolute expansion of mercury, to find the cubical expansion of the material forming a vessel.

Let the vessel have a narrow neck, and, if the

material be glass, let the neck be drawn out to a capillary point.

Let the weight of the empty vessel be w, and the weight when filled with mercury at 0° be W_0.

Let the temperature be raised to 100°, and let the weight of the vessel and the mercury which fills it at 100° be W_{100}.

Let a be the coefficient of absolute expansion of mercury, and K the mean coefficient of cubical expansion of the vessel between 0° and 100°.

Let v_0, v_{100} be the volumes of the vessel at 0° and 100° respectively, and let D_0, D_{100} be the densities of mercury at 0° and 100° respectively. Then, by the preceding formulæ,

$$v_{100} = v_0 \, (1 + 100 \, . \, K).$$

$$D_{100} \, (1 + 100 \, . \, a) = D_0.$$

$$\therefore \frac{v_{100}}{v_0} \frac{D_{100}}{D_0} = \frac{1 + 100 \, . \, K}{1 + 100 \, . \, a}$$

But the first of these expressions is the ratio of the weights of the mercury in the vessel at 0° and 100° respectively,

$$\therefore \frac{W_0 - w}{W_{100} - w} = \frac{1 + 100 \, a}{1 + 100 \, K}$$

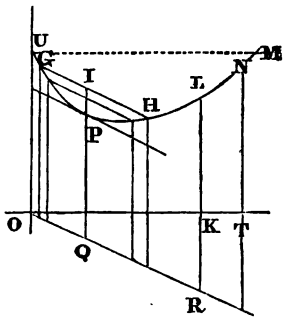
$$\therefore 100 \, K = \frac{W_{100} - w}{W_0 - w} \, (1 + 100 \, a) - 1$$

In the same way the mean coefficient of expansion between 0° and any given temperature may be found.

§ 26. Application of the Expansion Diagram to the case of water.

Let temperatures be denoted by distances measured along the line O T, and let O represent the temperature zero.

FIG. 19.



Take a glass vessel and let its capacity at 0° be taken as the unit of volume, and be represented by O U.

Draw O R such that the vertical distance between M U and O R at any point represents the capacity of the vessel at that temperature—that is to say, let the tangent of the angle T O R be the coefficient of cubical expansion for the glass vessel.

Set off above the line O T ordinates which represent the apparent volume of the water contained in the vessel. For instance, suppose the water to be contained in a flask fitted with a tube so as to form a water-thermometer; suppose the flask and part of the tube which is filled to contain as much water at 0° C. as would fill m inches of the tube, and suppose when the temperature is raised $t°$ the water rises n inches in the tube.

Then we take O K to represent $t°$, O U to represent m inches, and then K L on the same scale to represent $m+n$ inches.

Join the points determined in this way for a series

of temperatures. The line drawn will be a curve like the curve U N.

The true volume of the water at any temperature will be represented by the vertical distance between the lines O R and U N, at the point representing that temperature, and an inspection of the curve will show that the law of expansion is more complicated than that for most substances, and that there is a temperature of minimum volume, or, which is the same thing, a temperature of maximum density. This temperature may be found in the diagram by drawing a tangent to the curve U N parallel to the line O R, or by drawing a chord, G H, parallel to O R, near the point of contact, P, of this tangent, and then a vertical line, I P Q, through the middle point, I, of the chord, G H.

The point of maximum density has by this means been found to be 3·9°, or nearly 4° C.

§ 27. **Remarks specially applying to Gases.**—In considering the expansion of liquids and solids we do not find it necessary to take account of the pressure of the atmosphere upon their surfaces. A variation in this pressure does not affect the phenomenon of expansion in any perceptible degree. But the case is otherwise with gases. In the case of a gas, the variation of pressure causes changes of volume, of temperature, or of both. It is necessary, therefore, to investigate three distinct relations.

I. A relation between the volume and the pressure when the temperature remains constant.

II. A relation between the volume and the temperature when the pressure remains constant.

III. A relation between the pressure and the temperature when the volume remains constant.

These relations are given by the following laws :—

I. *Boyle's Law* (also called Marriotte's law).—At a given temperature the volumes v_1 and v_2, occupied by a gas, are inversely proportional to the pressures p_1 and p_2,

$$\text{or, } p_1 v_1 = p_2 v_2.$$

From this it follows that if d_1, d_2 be the density of the gas at the two pressures p_1 and p_2,

$$\frac{p_1}{d_1} = \frac{p_2}{d_2},$$

or the pressure of a gas is proportional to its density.

II. *Gay-Lussac's Law* (also called Dalton's law; the law was discovered by Charles).—If the same pressure be maintained all gases have the same coefficient of expansion, which is independent of temperature. Hence, if t_1 and t_2 be two temperatures defined by the expansion of dry air, the corresponding volumes v_1 and v_2 of a given quantity of gas are connected by the equation—

$$\frac{v_1}{1 + a t_1} = \frac{v_2}{1 + a t_2}.$$

From these two equations we can obtain a third and more general equation, which enables us to take account of simultaneous changes of temperature, volume, and pressure. We may suppose the whole change from the state indicated by v_1, p_1, t_1, to the state indicated by v_2, p_2, t_2, equivalent to two changes. We may suppose the final pressure p_2 attained while the

temperature remains at t_1; and if v' be then the volume, we have

$$v_1 p_1 = v' p_2.$$

Now we may suppose the temperature to be changed from t_1 to t_2, the pressure remaining at p_2, and the volume changing from v' to v_2.

Then, by the second equation,

$$\frac{v'}{1+a t_1} = \frac{v_2}{1+a t_2}.$$

Hence, by multiplying these equations together, and cancelling v', we have

$$\frac{p_1 v_1}{1+a t_1} = \frac{p_2 v_2}{1+a t_2}.$$

This one equation involves all the three relations mentioned above, for we have

(1) if $t_1 = t_2$, then $p_1 v_1 = p_2 v_2$;

(2) if $p_1 = p_2$, then $\frac{v_1}{1+a t_1} = \frac{v_2}{1+a t_2}$;

(3) if $v_1 = v_2$, then $\frac{p_1}{1+a t_1} = \frac{p_2}{1+a t_2}$.

§ 28. **Difference between vapours and permanent gases.**—Gases may be divided into three classes for the purpose of describing the exactness or inexactness of these laws. The gas which arises from the evaporation of a liquid at ordinary temperatures is termed a **vapour.** A gas which requires great pressure and cold to condense it, but which can nevertheless be condensed, is called a condensable gas.

Gases which have hitherto defied all attempts to condense them are termed permanent gases.

So long as vapours are in contact with the liquid from which they have arisen, an increase of the space containing them causes more evaporation, but no change of pressure. When, however, all the liquid has evaporated, any further increase in volume causes diminution of pressure. In proportion as a vapour under these conditions is allowed to expand, the pressure it exerts becomes more and more nearly inversely proportional to the volume occupied. Again, when a vapour not in contact with excess of liquid is heated, as the temperature rises the relation between volume, pressure, and temperature is more and more nearly expressed by the equation

$$\frac{p_1 v_1}{1+a t_1} = \frac{p_2 v_2}{1+a t_2}.$$

Hence, when vapours are sufficiently expanded, they obey the laws of Boyle and Gay-Lussac.

The condensable gases nearly obey the same laws at temperatures much above their points of liquefaction. From the fact that many gases which were once regarded as permanent have in recent years been liquefied, it seems natural to suppose that the gases of this third class, as oxygen, hydrogen, nitrogen, and nitric oxide, would be liquefied if we could command a lower temperature and greater pressure than has yet been secured; and that, on approaching their points of liquefaction, their properties would deviate from those expressed by the above laws, and would accord with those of vapours.

The properties of the permanent gases, such as dry air, oxygen, and hydrogen, are so nearly represented by the above formulæ that, except in cases when extreme accuracy is required, the accord may be considered perfect.

The agreement between the formulæ and fact, however, is found not to be rigorously exact in the case of any known gas when sufficiently delicate means are used to detect the difference.

The gradations in the amount of these deviations from the laws have led to the conception of an ideal gas, with which all others may be compared, and which obeys the two laws of Gay-Lussac and Boyle through all possible ranges of temperature and pressure. Such an ideal gas is termed a *perfect gas.*

§ 29. **Remarks on the Law of Gay-Lussac.**—The coefficient of expansion referred to in this law is the coefficient under constant pressure, or the amount by which the quantity of gas which occupies a unit of volume at 0° C. expands under constant pressure when its temperature is raised one degree. Regnault found this coefficient to be $\frac{1}{273}$ for dry air, and, assuming this to be the same for a perfect gas, the general formula becomes—

$$\frac{p_1 v_1}{1+\frac{t_1}{273}} = \frac{p_2 v_2}{1+\frac{t_2}{273}}$$

$$\text{or, } \frac{p_1 v_1}{273+t_1} = \frac{p_2 v_2}{273+t_2}.$$

Here the temperature t is supposed to be measured

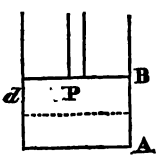
from a zero at the temperature of melting ice. Suppose now that, instead of counting degrees from the melting point of ice, we count them from a temperature 273° C. lower,—then the temperature of melting ice will be represented by 273°, that of boiling water by 373°, and the general formula may be written—

$$\frac{p\,v}{t} = \text{a constant.}$$

The zero of this scale of temperature is called, for reasons which will appear subsequently, the absolute zero of temperature. All we need to know at present about this point is that it is the zero of a scale of temperature, the adoption of which enables us to reduce the equation expressing the physical properties of gases to the simplest possible form.

§ 30. **Remarks on Boyle's Law.**—Let us suppose the gas to be contained in a cylinder closed by a movable piston, P, the area of which we may take as the unit of area. Then the whole pressure exerted by the gas on the piston, P, will be a measure of the pressure represented by p in the preceding formula. Suppose the piston loaded with weights, which may be reduced or increased at pleasure, and let the cylinder be vertical; then the weight of the piston, together with its load, including the pressure of the atmosphere above it, is equal to p.

FIG. 20.

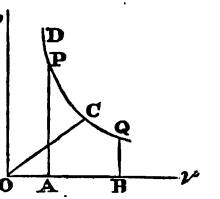


The volume of the gas is measured by the height, A B, for the area of a section of the cylinder is unity.

Now we can vary p by diminishing or adding to the load of the piston, and this can be done without altering the temperature, if we suppose the whole apparatus placed in a medium, as for instance, a large water bath kept at the same temperature. It is then found that the product p (A B) is constant.

Graphic representation of the Law.—Draw a horizontal line, O B, to represent the volume, and draw a curve, Q D, such that the ordinate, B Q, at any point, B, represents the pressure p which the gas exerts when it has the volume represented by O B, the temperature remaining unaltered (fig. 21). The curve, Q D, is characterised by the equation :

FIG. 21.



$$\text{O B} \cdot \text{B Q} = \text{a constant.}$$

This curve is known in geometry as a rectangular hyperbola, and has the following properties :—

(1.) The axes O v, O p, are asymptotes of the curve ; that is, they are straight lines to which the curve approaches as we travel along it from the point nearest O, but which the curve never meets.

(2.) If a tangent be drawn at any point P (see fig. 22) to meet the axes in M and N, and P K, P L be drawn through P perpendicular to the axes, then O L = L N, and O K = K M.

(3.) If O C bisect the angle O, the constant in the equation is proportional to the square on O C (fig. 21). But this product is proportional to t, the absolute

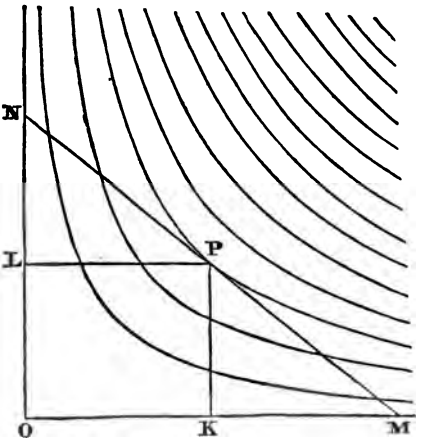
temperature (p. 62); hence o c is proportional to $\sqrt{t}$.

The equation to the curve may, therefore, be written:

$$p\,v = (\text{o c})^2 = k\,.\,t.$$

where k is constant.

FIG. 22.



(4.) If ordinates, P A, Q B, be drawn at two points, P and Q (fig. 21), then the area, P A B Q, is $c \log_e \frac{b}{a}$, where c is the constant for the curve, a=A P, and b=B Q. Hence, when the curve represents the changes in a gas, since $c = k\,t$,

$$\therefore \text{ Area P A B Q} = k\,t \log_e \frac{b}{a}.$$

(5.) Suppose the area to be divided into very narrow strips by vertical lines near together, and let v' be the distance between two adjacent lines, the length of the first of them being p, and its distance from the origin v. Then the area of this strip is $p\,v'$ or $c\,\frac{v'}{v}$ (since $p\,v = c$). Hence the whole area or the sum of the strips may be represented by $c \cdot \Sigma \frac{v'}{v}$. Conversely, the sum of a number of terms represented by $c \cdot \Sigma \frac{v'}{v}$ may be also represented by the area bounded by the rectangular hyperbola, and if, in the successive terms, v takes all values from a to b inclusive, the sum will be equal to $c \cdot \log \frac{b}{a}$.

§ 31. **Isothermal Lines.**—Let O A represent the volume v, occupied by a gramme of any given substance, and let A P represent the pressure p on its surface, per unit of area (fig. 21). Let the pressure change while the temperature t is kept the same. The volume diminishes as the pressure increases, so that the point P, whose position represents the relations of p and v, traces out a curve. This curve is called a line of equal temperature, or an *isothermal* line. If t be increased to $t+1$, and then kept at this value while p and v change, another isothermal line will be obtained. It is evident that by continuing the process the whole area in the figure may be mapped out by isothermal lines corresponding to temperatures which differ from one another by 1°. When the diagram is completed for any substance it is evident that, by the application

of a measuring scale, two out of the three quantities p, v, t, being given, the third may be found.

Isothermal Lines of Perfect Gases.—It was shown on page 64 that the equation connecting pressure and volume for a perfect gas is

$$p\,v = k\,t,$$

where k is a constant.

Let t also be constant, then we have as the equation to an isothermal line :

$$p\,v = \text{the constant } (k\,t).$$

The curve denoted by this equation is a rectangular hyperbola. By changing t in succession to $t+1$, $t+2$, &c., we obtain a series of isothermals as represented in figure 22.

To find the value of k we need only to know the pressure per unit of area, exerted by a unit of mass of the gas when occupying a unit of volume, at a given temperature. For instance, for air, which nearly resembles a perfect gas, the pressure per square centimetre exerted by 1 gramme at the temperature of melting ice, 273° C. above the absolute zero of temperature, is equal to the weight of 79,915 grammes when the air is confined in a cubic centimetre of space. Hence, with the centimetre, the gramme, and degree C. as units, $k = 79{,}915 \div 273 = 292{\cdot}7$

CHAPTER VI.

THE PRODUCTION OF HEAT BY FRICTION.

In this Chapter we take the first step towards an answer to the question—'What is heat?' We show that it cannot be a *substance*, for it may be generated, without limit, without any substance disappearing to account for its production. Expenditure of work will produce heat, and there is a fixed relation between the quantity of heat produced and the amount of work which is spent in producing it.

§ 32. **Experiments. Fifth Series.**—*Davy's Experiment.*—Davy, about 1798, caused two pieces of ice to rub against each other, and found that while the rubbing continued they were gradually melted.

Davy reasoned from this experiment as follows:—It is evident that ice by friction is converted into water, and as 'ice must have an absolute quantity of heat added to it before it can be converted into water,' and as the experiment is so arranged as to prove that the heat comes neither from the ice nor from surrounding bodies, it must be concluded that the heat is developed by friction.

Count Rumford's Experiments.—Having noticed in the boring of cannon at the Cannon Foundry at Munich that the metal became very hot, Count Rumford devised an experiment, in which the boring apparatus

was used without any other result than the production of heat. He caused a fixed blunt steel borer to be pressed into a hollow in a brass cylinder, revolving in a wooden vessel filled with water. While work was expended and the cylinder kept in uniform motion, the temperature of the water was found to rise continuously and regularly, until the water boiled. In one experiment with 18·77 lbs. of water initially at a temperature of 60° F., the temperature was raised regularly by 1° per minute, so that the water boiled in $2\frac{1}{2}$ hours. Count Rumford comments on his experiments thus: 'The quantity of heat produced equably, or in a continual stream (if I may use that expression), by the friction of the blunt steel borer against the bottom of the hollow metallic cylinder in the experiment under consideration, was greater than that produced equably in the combustion of nine wax candles, each $\frac{3}{4}$ of an inch in diameter, all burning together with clear bright flames.

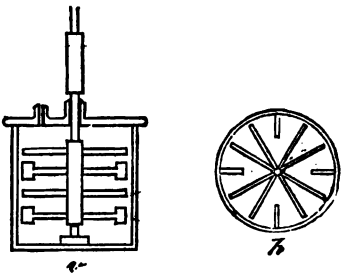
'As the machinery used in this experiment could easily be carried round by the force of one horse, these computations show how large a quantity of heat might be produced by proper mechanical contrivances, merely by the strength of a horse, without either fire, light, combustion, or chemical decomposition; and in a case of necessity the heat thus produced might be used in cooking victuals.

'In reasoning on this subject we must not forget to consider that most remarkable circumstance, that the source of the heat generated by friction in these experiments appeared evidently to be inexhaustible. It is hardly necessary to add, that anything which any

insulated body, or system of bodies, can continue to furnish without limitation, cannot possibly be a material substance; and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in these experiments, except it be MOTION.'

Joule's Experiments.—On friction of Water.—This set of experiments consisted in setting water in motion

FIG. 23.

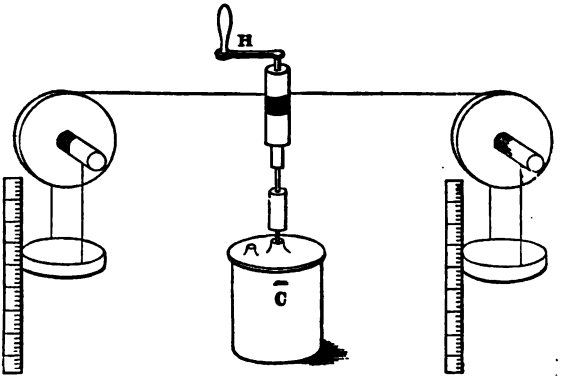


by means of a brass paddle-wheel, and noting the rise of temperature produced by the friction of the water on itself, and on the fixed surfaces in the copper vessel which contained it.

A vertical section (*v*) and a horizontal section (*h*) of the apparatus are shown in the figure (fig. 23). The paddle-wheel consisted of a vertical axle and eight pairs of brass vanes. The axle was made in two parts, both of brass, connected by wood so as to prevent loss of heat by conduction. The paddle-wheel worked between four pairs of fixed vanes attached to

the framework of brass which supported the socket for the axle. The whole of this system was placed in a copper vessel, capable of containing about 7 kilogrammes, or 1½ gallon, of water, and covered by a lid with two apertures, one for the axle of the paddle-wheel, and the other for the thermometer. The vessel rested by as few points of support as possible on a

FIG. 24.



wooden stand, and was protected from radiation by a screen. The motion of the paddle-wheel was caused by the descent of two equal leaden weights suspended by cords from the axles of two exactly equal wooden pulleys, the axles being 2 inches in diameter and the pulleys 1 foot (fig. 24). The pivots were of steel, and rested on friction wheels similar to those used in Atwood's machine.

The mode of experimenting was as follows. The

weights were drawn up, and while they were held at rest by the handle, H, the temperature of the water was determined by a delicate thermometer, giving the hundredth part of a degree Fahrenheit. The handle was then liberated, and the weights fell until stopped by the floor. The weights were then wound up again and allowed to fall as before. This having been done twenty times the temperature of the apparatus was again determined. The temperature of the air in the laboratory was noted at the beginning, in the middle, and at the end of the experiments, which lasted thirty-five minutes, and the result used in making corrections for radiation. In the last part of their fall the velocity of the weights was observed to be nearly uniform, and its value was determined by direct observation. If W be the weight, h the height of its fall, and v its velocity on reaching the ground, then the work expended in overcoming the resistances is evidently $Wh - \frac{1}{2}\frac{W}{g}v^2$.

Experiments on Mercury.—The apparatus above described was slightly modified for the use of mercury instead of water. The copper vessel was replaced by a cast-iron one, and the number of vanes to the paddle-wheel was reduced to six pairs, while the number of fixed vanes was increased to eight pairs.

Experiments on Cast-iron.—In the experiments on iron the vertical axis carried a bevelled cast-iron wheel, against which another bevelled wheel was pressed by a lever. The heat produced was measured by observing the quantity of heat given to a known quantity of water in which the apparatus was immersed.

After making corrections for radiation, conduction.

and the friction of the pulleys, Joule arrived at the following conclusions:

1. That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the work expended, and the proportion is independent of the nature of the surfaces between which the friction takes place.

2. That the quantity of heat capable of increasing the temperature of 1 lb. of water at 60° F. by 1° F., can be evolved by the expenditure of mechanical work represented by the fall of 772 lbs. through the space of 1 foot; or the quantity of heat capable of increasing the temperature of 1 gramme of water by 1° C. can be evolved by an expenditure of work which could raise 423·55 grammes through a height of 1 metre.

The possible errors in the results obtained in the experiments on water are so small that we must accept the number 424 as a very close approximation; and this has been confirmed by other experimenters, although no other experiments have exceeded Joule's in precision and uniformity of result.

§ 33. **Remarks on the Experiments.**—Let us revert for a moment to a proposition on the theory of energy of a system of bodies, given on page 6.

In every machine in motion, the work given in any time is equal to the work done by the machine *plus* the gain of work accumulated in the moving parts. If the machine has arrived at its state of uniform motion, so that there is no gain in the work accumulated, then the work given must equal the work done by the machine.

This equality does not, however, hold good if we consider simply *useful* work done by the machine; for instance, consider a machine in which the work given and the work done are of the same kind; for example, suppose the machine to be a water-mill, used to pump water. It is always found that the work done is only a fraction of the work expended in moving the machine. Thus, if the mill is turned for a given time by the fall of a weight W_1 of water from a height h_1, the water moving after the fall with the same velocity as before, and if the mill in the same time pumps up a weight W_2 of water to a height h_2 above its first level, then the work $W_2\ h_2$ is never greater, even in the most perfect machines, than two-thirds of $W_1\ h_1$, the work spent in moving the mill.

Similarly, whenever we have the means of measuring the work done by the moving forces, and the work accomplished by the machine, we find that the first exceeds the second. The difference is usually accounted for by admitting, amongst the forces to be considered, the friction which occurs between contiguous surfaces having unequal velocities.

But, whenever friction occurs, the material composing the rubbing surfaces is found to be heated, and the heating effect increases with the friction. The heating of one part of the machine does not occur at the expense of the heat in another part, for no corresponding cooling is observed; but there is an absolute creation of heat in the parts which are rubbed together. In most cases, the friction of rough bodies moving in contact is accompanied by a wearing or modification of the surfaces, but it is possible

to lessen indefinitely all other changes than the elevation of temperature, and to regulate the applied forces so that the machine moves with uniform velocity. When these conditions are secured, the causes and consequences in operation are reduced to the expenditure of work by the applied forces, and the heating of the substances composing the rubbing surfaces. If the friction be diminished while the work of the applied forces, in a given time, remains the same, the machine no longer moves uniformly, and kinetic energy is accumulated in the moving parts. Hence the work of the applied forces may produce either an increase of kinetic energy in a quantity of matter, or a quantity of heat. Now we know that in the first case there is equality between the applied work and the increase of energy, and we are, therefore, naturally led to enquire whether, in the second case, there is a definite relation between the applied work and the amount of heat produced.

The methods used by Joule in his experiments on friction, described in pages 69 to 71, gave him the means of measuring, at the same time, the heat produced and the work expended in overcoming friction.

The final result, which has been already stated in a slightly different form (p. 72), was that each unit (metre-gramme) of work spent in overcoming friction produces $\frac{1}{424}$th of a unit (gramme-degree)[1] of heat; or, that the number 424 is a constant multiplier by which the number of units of heat produced must be

[1] A *gramme-degree*, or, more explicitly, a *water-gramme-degree*, is a convenient term for the quantity of heat needed to raise the temperature of a gramme of water one degree.

multiplied to obtain the number of units of work expended in the production of the heat.

The ratio of the work expended to the heat produced is termed the *Dynamical Equivalent of Heat.* We will represent it by $\mathcal{J}$. Hence if a quantity of work, W, be given to a machine, and the only result be a production of a quantity of heat, H, at the rubbing surfaces, then :

$$W = \mathcal{J} H.$$

It would be possible to do with this equation what is done in dynamics with the equation connecting force and acceleration, and in other cases where two variables have a constant ratio, namely, to choose the units so that this ratio shall always be equal to unity. We might, for instance, take for the unit of heat the heat produced by the expenditure of a unit of work. If, however, we fix arbitrarily the units both of work and heat, then the constant $\mathcal{J}$ will have a value determined by the units chosen. When the unit of work is the kilogrammetre, and the unit of heat the heat required to raise the temperature of a kilogramme of water from 0° to 1° C., then $\mathcal{J} = 424$ nearly; when the unit of work is the foot-pound, and the unit of heat that required to raise the temperature of 1 lb. of water from 0° to 1° C., then $\mathcal{J} = 1{,}390$; and, with the same units as in the last case, except that change of temperature is measured in degrees Fahrenheit, $\mathcal{J} = 772$.

It is important to remark that, in each of the above cases, the unit of force which enters into the definition of the unit of work is the force of gravity acting upon

a certain quantity of matter; and that, as the intensity of gravity varies at different parts of the earth's surface, to the extent of about $\frac{1}{2}$ per cent. of its whole amount, the kilogrammetre, or foot-pound, or any other unit of work founded upon the weight of a given mass varies in like manner. When the dynamical equivalent of heat has been measured in terms of the gravitation-unit of work at a given place, the corresponding value expressed in absolute units of work can be obtained by multiplying the result by the number of absolute units of force in the weight of unit mass at the place where the measurement was made. Thus, Joule's experiments give $\mathcal{J}=42{,}355$ centim. grammes at Manchester, where the weight of a gramme is 981·3 centim.-gram.-second units of force (§ 4); hence in absolute measure $\mathcal{J}=42{,}355\times 981{\cdot}3$ $=41{,}560{,}000$.

We may now modify the equation of work in a machine to suit the case of heating by friction. If $W=$ the work expended on the machine in a given time; $U=$ the useful work done by the machine in the same time; $K=$ the increase of kinetic energy in the moving parts; $H=$ the heat produced between rubbing surfaces; then

$$W=U+K+\mathcal{J}.H.$$

CHAPTER VII.

THE STEAM-ENGINE.

In this Chapter we have to examine, by means of experiments on the steam-engine, changes which are the exact converse of those investigated in Joule's experiments, and the other experiments described in Chapter VI., on the generation of heat by the expenditure of work; that is to say, we have to show that when heat is expended in the production of work, there is a constant ratio between the amount of heat expended and the amount of work done.

§ 34. **Experiments. Sixth Series.**—To prove that when saturated steam expands, doing work, a portion of it liquefies (Hirn).

A copper cylinder, about 6 feet long and 6 inches in diameter, has its ends closed by thick but transparent glass. It has two stop-cocks, one of which may connect it with the air, and the other with the cylinder of a steam-engine. At first the stop-cock communicating with the air is partly opened, and that communicating with the cylinder is completely open. The steam drives out the air and fills the cylinder with saturated vapour. The vessel is then seen to be perfectly transparent. The stop-cock communicating with the atmosphere is now completely opened. The

steam expands, some of it escaping by overcoming the atmospheric pressure, and at the same time a cloud is seen to form in the cylinder which renders it opaque. This proves that with saturated steam condensation accompanies expansion.

§ 35. **The Steam-Engine.**—The essential parts of an ordinary steam-engine are:

(1.) The Boiler. By the heat of combustion of the fuel, the boiler and its contents are kept at a nearly constant temperature above 100°, and consequently the space above the water is always occupied by steam at a constant pressure, greater than that of the atmosphere.

(2.) The Condenser. This is a vessel kept free of air by a pump worked by the engine and maintained at a low temperature by a jet of cold water admitted into it, or by being simply surrounded with cold water. Consequently, the pressure within the condenser is that which saturated aqueous vapour exerts at a temperature considerably below 100°, and is therefore always much less than that of the atmosphere.

(3.) The Cylinder, fitted with a Piston attached to a rod which passes steam-tight through one of the plates which close the ends of the cylinder.

To set the engine at work, communication is made between the boiler and one end of the cylinder, and between the condenser and the other end. The two surfaces of the piston are thus exposed to pressures which depend upon the temperatures of the boiler and condenser respectively, and the piston is urged towards one end of the cylinder with a force corre-

sponding to the difference of these pressures. When the piston gets to the end of its stroke, the communications between the boiler and condenser respectively and the cylinder are inverted, and the piston is therefore urged with the same force as before towards the opposite end; then a second inversion of the communications causes the piston to be driven in the same direction as at first, and, the actions just mentioned being repeated over and over again, a continuous reciprocating motion of the piston is kept up.

§ 36. **The Relation between Heat and Work in the Steam-Engine.**—Let us inquire what passes while the piston makes one stroke. Cold water is heated in the boiler until it becomes saturated steam above 100° C.; some of the steam then enters one end of the cylinder, and drives the piston to the other end; this quantity of steam next passes to the condenser, and is reconverted into water (which may be afterwards returned to the boiler, to go through the same course again), while another portion of steam enters the opposite end of the cylinder and forces the piston back to its original position. In a complete cycle of operations, not only do the pieces of the mechanism return to the same relative positions, and, when the machine is working uniformly, with the same velocities, but the working agent itself returns to its initial state.

There are, however, three phenomena connected with the action which are progressive and continuous, and which are not reversed so as to leave everything exactly in its initial state. In the boiler the water, in becoming steam, takes up heat, which the steam

carries to the cylinder. The piston at every stroke does work; the steam which passes to the condenser gives up heat to the water used to condense it. Now, what is there to account for the constant performance of work by the piston? Is there a difference between the quantity of heat taken up in the boiler and the quantity given out in the condenser? If so, is there a fixed relation between this difference and the amount of work done? These questions have been answered by experiments made by Him, a civil engineer of Colmar, who, applying to the purposes of his experiments the material resources of a very large manufactory, through a considerable period of time, measured the amounts of heat taken in and given out, and the work done by engines of 100 to 200 horse-power.

Him found that less heat was conveyed to the condenser than was carried from the boiler, and the number which he obtained for the ratio of the work done to the heat which disappears was very nearly the same as that obtained by Joule as the result of experiments on friction.

To measure the quantity of heat carried from the boiler for a given number of strokes of the piston.—Let us suppose the engine to have arrived at a uniform speed. We require to observe:

(1.) The quantity and temperature of the water consumed.

(2.) The temperature of the steam produced.

(3.) The pressure of the steam produced.

The first may be measured by causing the water to be supplied at such a rate as to keep it at the same level in the boiler, and measuring the quantity and

temperature of the water supplied. The second and third particulars will of course be furnished respectively by a thermometer and a manometer attached to the boiler.

We require to know in addition the latent heat of evaporation. A complete table for different temperatures has been furnished by the researches of Regnault, and a formula has been deduced from this table for the quantity of heat required for the evaporation at a given temperature of a unit of mass of water. Suppose the water to be originally at the temperature 0° C. or 32° F. Then, for every pound of water, we have for the total quantity of heat needed to raise it to $t°$ and evaporate it at that temperature:

$$Q_1 = 606{\cdot}5 + {\cdot}305\, t \text{ (Centigrade)};$$

or
$$Q_1 = 1091{\cdot}7 + {\cdot}305\,(t - 32°) \text{ (Fahr.)},$$
$$= 1082 + {\cdot}305\, t.$$

To measure the quantity of heat, Q_2, conveyed to the condenser in the same number of strokes.—For this purpose we must know:

(1.) The quantity, w, of cold water carried into the condenser to condense the steam brought there;

(2.) The temperature, θ_1, of this water; and,

(3.) The temperature, θ_2, to which the water of the condenser is raised by the condensation of the steam.

Taking the specific heat of water as unity, which experiment shows will involve but a very small error between the limits of temperature used in the steam-engine:

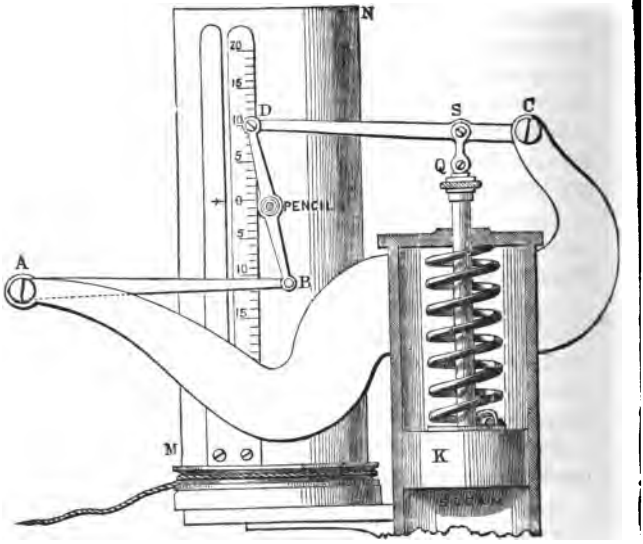
$$Q_2 = w\,(\theta_2 - \theta_1).$$

To measure the work done in the same number of strokes.

Richards's Indicator.—This instrument consists of:

(*a.*) A small cylinder, containing a piston, K, and connected with the cylinder of the steam-engine by a pipe which allows the steam to pass to the part below

FIG. 25.



the piston, K. In consequence of this connection the steam presses on the lower side of the piston, K, with the same pressure as on the piston in the working cylinder of the steam-engine. A spiral spring presses on the upper side of the piston, K, and its elasticity counterbalances the pressure of the steam below; as this pressure increases the piston rises, and the spring is com-

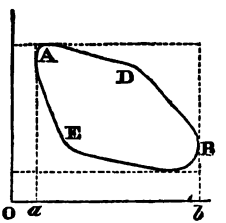
pressed until its reaction is increased to the same extent.

(*b.*) A larger vertical cylinder, M N, covered with white paper, and capable of turning about its axis. This cylinder is connected with the working parts of the engine in such a way that it turns as the piston of the engine moves, and any point on it passes in any given time through a space proportional to that through which the piston moves in the same time.

(*c.*) A pencil, the point of which presses against the paper on the cylinder, M N, and which moves up and down with the piston, K. The rectilinear motion of the pencil is secured by placing it at the middle point of a rod, B D, the middle one of three rods, A B, B D, D C, jointed together at B and D, and to fixed points at A and C. The point of the pencil, if its range be not too great, moves in a vertical straight line.

If the cylinder, M N, be connected with the engine while the steam is shut off from K, the pencil will trace on the paper a horizontal line, termed the line of no pressure. If steam be admitted below the piston K, then the line traced will be a curve, which when the engine works regularly, so that each stroke is in all respects a repetition of the one before it, will be a closed curve as in the figure (fig. 26).

FIG. 26.



In order to calculate from the figure the work done we must find out the scale upon which the figure is drawn. For this purpose two sets of observations are

necessary, one to determine the scale for horizontal measurements which represent the distances moved through by the piston, and the other to determine the scale for vertical measurements which represent pressures. To determine the first it will be necessary simply to measure the range of the piston, and to remark that this range is represented by the extreme breadth, *a b*, of the figure. Equidistant vertical lines divide this interval into equal parts. We may find the scale of pressures by connecting the indicator with a manometer and forcing syringe, by means of which any given pressure of air or steam may be produced on the piston, K, and at the same time the pressure can be measured in inches of mercury. This may be done once for all for the same indicator, and the result marked on a scale permanently attached to the cylinder, M N, as in the figure. Knowing the scales on which the indicator diagram is drawn, we can now find its area, and so obtain, as explained in § 2, the measure of the work done by the engine in each stroke.

§ 37. **Results of Hirn's Experiments on the Steam-Engine.**—After making corrections as far as possible for loss of heat by radiation and conduction, Hirn found that:

(1.) The quantity of heat, Q_1, carried from the boiler to the cylinder always exceeds the quantity, Q_2, carried from the cylinder to the condenser.

(2.) The difference $Q_1 - Q_2$ is proportional to the external work done by the engine:

$$\text{or } Q_1 - Q_2 = \mathcal{J} W,$$

where $\mathcal{J}$ is a constant.

As the mean of many experiments Hirn found for J the value 414, which, considering the difficulty of eliminating errors in the experiments, is so near to that found by Joule, by a converse process, that we may conclude that heat and work are mutually convertible according to a fixed ratio.

This fact constitutes what is generally known as the First Law of Thermodynamics, which may be enunciated as follows:

§ 38. **First Law of Thermodynamics.**—When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or spent in producing purely thermal effects, equal quantities of heat are put out of existence or are generated.

In proof of the law we have:

(1.) The experiments of Joule and others on the production of heat by the expenditure of work.

(2.) The experiments of Hirn and others on the performance of work through the expenditure of heat.

(3.) Experiments and calculations (to be subsequently described) on the properties of air and other gases, which enable us to calculate, within a very small range of possible error, the numerical constant for the ratio of the units of work and heat.

(4.) The fact that by assuming the law we are able, from the observed properties of bodies, to predict other properties not at first evident, but which experiment afterwards proves to be true. Cases illustrating this remark will be given in a subsequent chapter.

§ 39. **Proposition.**—When the absorption or emission of a quantity of heat by a material system is attended only by a variation in the energy of the

system, the ratio between the amount of change in the energy of the system and the corresponding quantity of heat is constant; in other words, there cannot be two values of the dynamical equivalent of heat.

Consider two machines, A and B, in the first of which work is transformed into heat, and in the second of which heat is changed into accumulated work. For instance, A may be a machine producing heat by friction, and B a steam-engine with heavy fly-wheel.

Let $\mathcal{J}$ be the dynamical equivalent for the machine A, so that, if W be the amount of work which in one complete cycle of operations produces the quantity of heat Q, then:

$$W = \mathcal{J} Q.$$

Let Q be used to work the engine B, and, if possible for this engine, let $\mathcal{J}'$, the dynamical equivalent of heat, be not equal to $\mathcal{J}$. The work accumulated in B will be:

$$W' = \mathcal{J}' Q = \frac{\mathcal{J}'}{\mathcal{J}} W.$$

Let this quantity of work be expended on the machine A. It will produce heat Q', such that:

$$\mathcal{J} Q' = W'.$$

If Q' be used on B, work will be accumulated equal to $\mathcal{J}' Q'$;

$$\text{but } \mathcal{J}' Q' = \frac{\mathcal{J}' W'}{\mathcal{J}} = \left(\frac{\mathcal{J}'}{\mathcal{J}}\right)^2 W.$$

Similarly after n, complete periods, all parts of the

machines occupying the same positions as at the beginning, the accumulated work will be:

$$\left(\frac{\mathcal{F}'}{\mathcal{F}}\right)^n W.$$

If $\mathcal{F}'$ be less than $\mathcal{F}$, when n increases indefinitely this diminishes indefinitely, that is to say, the system tends continually to a condition of rest without there being any physical change in its constitution, which is contrary to the first law of motion. If $\mathcal{F}'$ be greater than $\mathcal{F}$, when n increases indefinitely the accumulated work increases indefinitely, and all the particles of the system may return exactly to the same positions as at the beginning, in exactly the same physical condition, but with an accumulated kinetic energy indefinitely great, which contradicts the principle of energy stated on page 6. Hence $\mathcal{F}$ and $\mathcal{F}'$ cannot be unequal.

§ 40. **General Remarks.**—*Some conditions necessary for the production of work by the expenditure of heat.*—We may now use our knowledge of the steam-engine to illustrate some properties of all heat-engines. In the first place it is necessary for the continuous performance of work by the expenditure of heat that we should have bodies of different temperatures. We can no more do work by using the heat in bodies all having the same temperature, than by the action of gravity on bodies in contact with the earth's surface. The continuous performance of work by a heat-engine is always attended by the transfer of heat from a hotter to a colder body; it is evident, therefore, that the power of turning heat into work depends in some way on the temperatures of the two bodies.

§ 16. E
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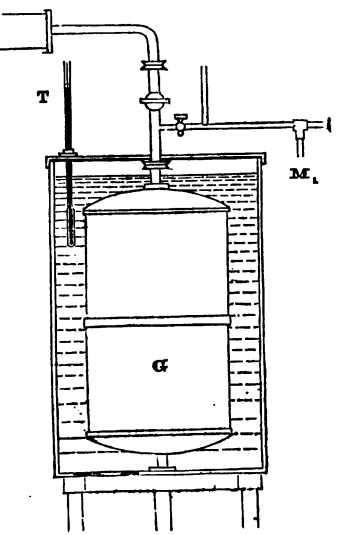
CHAPTER VIII.

SPECIFIC HEATS OF GASES.

§ 41. **Experiments. Seventh Series.**—*Experiment I.—Apparatus used by Regnault to determine the specific heat of a gas.*—This apparatus may be divided into four principal parts.

FIG. 27.



(1.) *The gas holder*, G. The gas when purified and dried is compressed into a large vessel, G, placed in a large bath of water, the temperature of which is indicated by a thermometer, T. The vessel, G, is connected with a manometer, M_1, to show the pressure of the gas in it (fig. 27).

(2.) *The regulator*, R (fig. 28). The gas flows from G through a tube

If two bodies having different temperatures are connected by a conductor of heat—a bar of copper for example—heat passes from the hot body to the cold body without doing work. When heat passes by conduction or radiation between two bodies, not only is no external work effected, but the power of turning heat into work which is possessed by the bodies in consequence of the difference of temperatures is permanently lost. Something else is necessary, therefore, in addition to the two bodies of different temperatures.

The third requisite is an intermediate body capable of changing its volume on the application of heat. This body must be placed first in contact with the hot body so that it takes in heat, and then carried to the cold body, to which it gives out heat. By the changes of volume, produced by taking in and giving out heat, work may be done. In the steam-engine the hot body is the boiler, the cold body the condenser, and the intermediate body the water changed into steam.

It is evident also since heat is wasted, as far as the production of work is concerned, when it passes between bodies at different temperatures by conduction, that the engine will be most effective when the intermediate body is at the same temperature as the hot body while it takes in heat, and at the same temperature as the cold body while it gives out heat. This may be called *the condition of maximum efficiency*, and will be discussed more fully as we develop the general theory of heat-engines. We will call the three essential parts of a heat-engine, the source, the refrigerator, and the intermediate body.

CHAPTER VIII.

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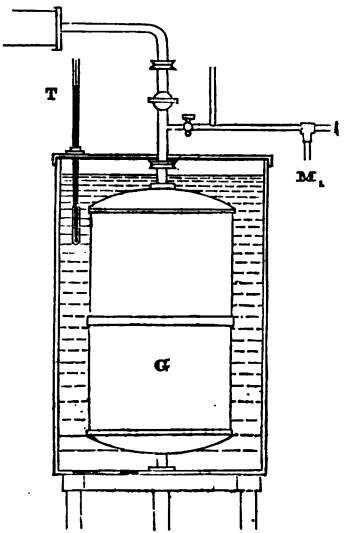
FIG. 27.



(1.) *The gas holder*, G. The gas when purified and dried is compressed into a large vessel, G, placed in a large bath of water, the temperature of which is indicated by a thermometer, T. The vessel, G, is connected with a manometer, M_1, to show the pressure of the gas in it (fig. 27).

(2.) *The regulator*, R (fig. 28). The gas flows from G through a tube

the aperture in which, at one point, can be enlarged or contracted at will by a contrivance termed the regulator. This consists of a metal cylinder moving in a tube of rather larger diameter than itself, and attached to a screw by which it may be forced into or withdrawn from the tube. Near the regulator is a second manometer, M_2, containing oil instead of mercury, since it has to indicate a pressure only slightly in excess of the atmosphere. By turning the screw in the regulator the aperture can be altered by hand until the indication of the manometer, M_2, remains stationary, and, when this is the case, the current has evidently a constant velocity.

FIG. 28.

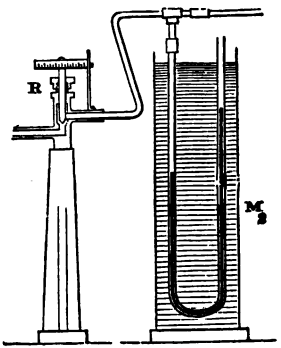
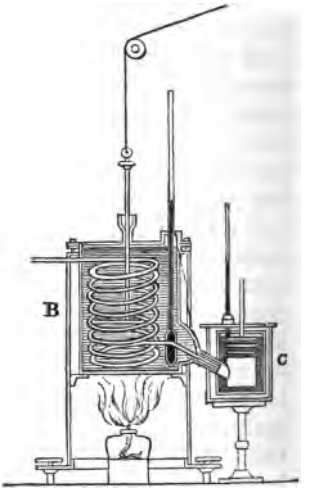


FIG. 29.



(3.) *The oil-bath*, B. The gas is heated to a high temperature by passing along a tube arranged in spiral

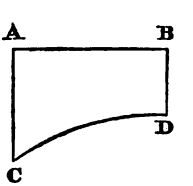
form in a bath of oil B, furnished with stirring-ring and thermometer (fig. 29).

(4.) *The calorimeter*, C. Finally the gas flows through a tube folded so as to present as much surface as possible to the water in a calorimeter.

Remarks respecting the apparatus used by Regnault to determine the specific heat of a gas.—The methods which have been indicated for finding the specific heats of solids and liquids apply also to gases, the most convenient method being in all cases the method of mixtures. There are, however, difficulties in the way of the experiment when applied to a gas which necessitate more elaborate apparatus.

First, the readiest way of conveying the gas from the vessel in which it is heated, to the calorimeter in which it delivers up its excess of heat, is to allow it to flow through a continuous tube. The portion of the tube coiled in the heating vessel and that in the calorimeter must be so long that the gas will always acquire in succession the temperatures of these vessels. In order to find the specific heat of the gas we must divide the quantity of heat given to the calorimeter by the product of the mass of the gas by the fall of temperature. But in this case the temperature of the calorimeter is constantly rising, so that the fall in the temperature of the gas is less and less. If we measure off along A B (fig. 30) lengths proportional to the masses of the gas which have passed through at different instants, and take

FIG. 30.



A C, perpendicular to A B, to represent the difference of temperature between the heating vessel and cooling vessel at the commencement, and let C D be such a curve that the ordinate at any point represents the difference of temperatures, when the amount of gas represented by the abscissa at that point has passed, then, by a principle we have already frequently used, the area A C D B represents the product required. If the gas passes with uniform velocity the calculation of the area becomes easy, for then evidently C D is a straight line. If A B $= m$, A C $= T - t_1$, B D $= T - t_2$,

$$\text{the area A C D B} = m\left(T - \frac{t_1 + t_2}{2}\right).$$

Let $H = C + R - K$. Where C is the total increase of heat in the calorimeter, R the heat lost by radiation, K that gained by conduction from the heating vessel. Let s = the specific heat: then—

$$H = m\,s\left\{T - \frac{t_1 + t_2}{2}\right\}.$$

The object of the regulator R, in the preceding experiment, is to cause the current to be constant, hence it also causes the preceding equation to take the simple form here given to it.

§ 42. **Discussion of the Experiments.**—In considering the relation between the amount of heat given to a body and the change of temperature produced in the case of solids and liquids, it was not necessary to notice the change of volume which almost invariably attends the change of temperature; for the change of volume is very small, especially in solids, and we

have no means of controlling it to any appreciable extent.

In studying the calorimetric properties of gases it is necessary to note the simultaneous changes of volume, pressure, and temperature. Before we can determine the quantity of heat which must be given to a gas to change it from one state to a second state, in which the volume, pressure, and temperature are all different from those of the first state, we must examine the three cases obtained by making in succession each of the three quantities constant, exactly as was done in considering Boyle and Gay-Lussac's laws (see § 27). For instance, we must find equations for the quantity of heat required to produce :

(1.) Given changes of volume and pressure, the temperature being constant.

(2.) Given changes of volume and temperature, the pressure remaining constant.

(3.) Given changes of pressure and temperature, the volume remaining constant.

As, in the first case, the heat required does not change the temperature, we will regard it as a kind of latent heat ; in the second and third cases we are introduced to two kinds of specific heat.

Latent heat of Dilatation.—Imagine a unit of mass of a gas to be confined in a vessel of good conducting material, and to be placed in a bath which can be kept at a constant temperature. Let v be the volume occupied by the gas at first, and let the volume be then increased by a small quantity, v' ; heat will pass through the conducting materials of the vessel. Let q' be the quantity of heat which the gas requires to

enable it to change its volume from v to $v+v'$ without change of temperature, then the ratio (or more exactly the limit of the ratio), $\frac{q'}{v'}$ is the *latent heat of dilatation.* Let this ratio be denoted by M, hence

$$q' = Mv' ;$$

or, in other words, Mv' is the quantity of heat absorbed while the volume changes by a *very small* amount, v', the temperature remaining constant.

Specific heat with constant pressure.—Let a unit of mass of a gas be kept under constant pressure ; for instance, suppose the gas to be confined in a cylinder fitted with a movable air-tight piston, loaded with a given load. Let a small quantity, q', of heat, absorbed at a temperature t, raise the temperature from t to $t+t'$ where t' is small, then the ratio $\frac{q'}{t'}$ (more exactly the limit of this ratio), is termed the *specific heat with constant pressure* at the given temperature. Let it be denoted by K. Then the quantity q' of heat absorbed in raising the temperature of a gas through a very small range, t', the pressure being constant, is Kt'.

Specific heat with constant volume.—Finally imagine the volume occupied by the gas to remain invariable, while the temperature and pressure receive small increments. Let a small quantity, q', of heat given to a unit of mass of the gas raise the temperature from t to $t+t'$, then the ratio (or more exactly the limit of the ratio), $\frac{q'}{t'}$, is termed the *specific heat with constant*

volume at the given temperature t. Let it be denoted by N. Then, if a unit of mass of a gas have its temperature raised through a very small range, t', while the volume remains unchanged, the quantity of heat absorbed is Nt'.

The values of K for air and other gases have been carefully determined by Regnault by means of the apparatus described at the beginning of this chapter; but the difficulties in the way of determining N by direct experiment have not yet been surmounted. We shall return to the theoretical determination of the ratio of K to N, and hence the calculation of the value of N, in a subsequent chapter.

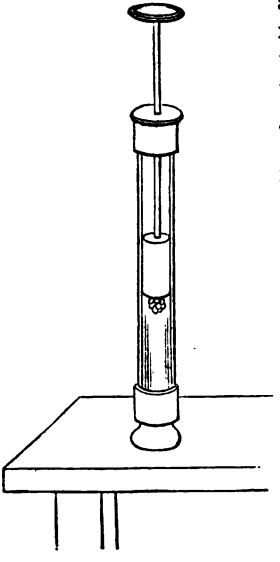
That Regnault's method satisfactorily solves the difficult task of determining the specific heat of gases under constant pressure, is shown by the fact that the results obtained by him for the permanent gases agree with what we have already seen (Chapter III.) ought to be the case. On tabulating the results of the experiments, it was found that the specific heat of any permanent gas does not vary with changes of temperature and pressure. For instance, whatever the temperature and pressure, one pound of air in cooling through the same number of degrees of temperature always gives out the same quantity of heat. But the specific heat of any gas which does not obey Boyle's and Gay-Lussac's laws increases with the temperature.

CHAPTER IX

EXTERNAL AND INTERNAL WORK.

§ 43. **Experiments. Eighth Series.**—*Experiment I.* —*The air-syringe.* —The air-syringe is a cylinder fitted with an air-tight piston. It is used to show that the compression of air generates heat. If a piece of German tinder be placed in a small cavity at the end of the piston, on quickly forcing in the piston an elevation of temperature may be obtained sufficient to ignite the tinder (fig. 31).

FIG. 31.



Experiment II.—If air is compressed in a vessel closed by a stop-cock, and is then allowed to escape, the air is cooled. By slowly condensing the air in a copper vessel, allowing the heat produced by the compression to pass away by conduction and radiation,

and then, having placed the vessel in a bath of water, suddenly allowing the confined air to escape, repeating the experiment several times, the temperature of water has been reduced to 0° C., and ice has been formed.

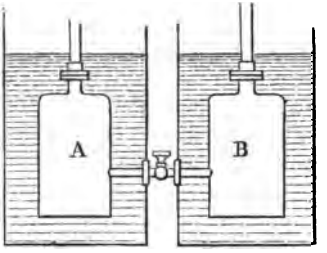
This experiment is made on a large scale in the mines of Schemnitz, where, in connection with an apparatus for raising water, air saturated with moisture can be confined in a chamber under a pressure of nine atmospheres (i.e. under the pressure of a column of water 260 feet high). On turning a tap which liberates the air its temperature falls considerably, the contained moisture descends in the form of snow, and the mouth of the tap becomes covered with ice.

Experiment III. (Gay-Lussac).—Two air-pump receivers, A and B, are screwed together, and a delicate thermometer is inserted in each. One of them, B, is wholly or partially exhausted, while the other contains air at the normal pressure. On opening the communication between A and B, so that air rushes from A to B, the rarefaction produced in A is attended by a fall of temperature, and the condensation of air in B is attended by a rise of temperature. The fall indicated by one thermometer is found to be equal to the rise indicated by the other.

Experiment IV. (Joule).—Two copper receivers, A and B, are connected by a tube and stop-cock, and are placed in separate water-calorimeters containing equal weights of water (fig. 32). Air is condensed in A to a pressure of twenty-two atmospheres, and B is exhausted. When the communication between A and B is opened, the gas is divided equally between them,

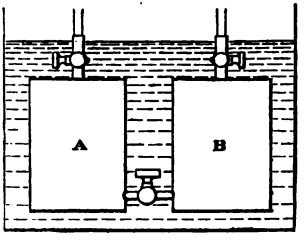
and the pressure in each becomes eleven atmospheres. It is found that the temperature of the water about B is raised, and that of the water about A falls, but the quantity of heat lost by one calorimeter is exactly equal to that which is gained by the other.

FIG. 32.



If now the two receivers be placed in the same water-bath (fig. 33), and the experiment repeated, the temperature of the water remains unchanged, there being on the whole neither absorption nor liberation of heat. The experiment shows that gas cools in expanding, but that, when no external work is done, this effect is exactly compensated by the heat which is disengaged through the friction of the gas, and the impacts which destroy the velocities communicated to the particles of gas while it is expanding.

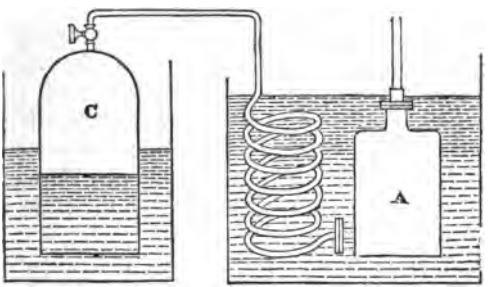
FIG. 33.



Experiment V. (Joule).—The receiver, A, containing gas condensed to two atmospheres, is placed in a calorimeter and is connected with a gas-holder, C, at

first filled with water and inverted in a water-bath (fig. 34). The gas passes from A to C, along a thin spiral tube almost entirely immersed in the same water as the receiver A. When the communication between the vessels is opened, the gas from A flows along the tube, depresses the water in the gas holder, and divides itself between the vessels, so that the pressure is reduced to one atmosphere. The loss of heat experienced by the calorimeter is found to be

FIG. 34.



proportional to the work done in driving down the water in the gas-holder against the pressure of the atmosphere.

§ 44. **Discussion of the Experiments.**—The first question which meets us in attempting to find relations between the heat given to a gas and the work it does in consequence, is this: 'How shall we determine what amount of heat the gas requires to enable it to occupy a larger space? When a body visibly changes state, heat is absorbed without affecting the body's temperature. To change ice into water heat is

required, which neither does external work nor raises the temperature of the substance; similarly, to turn water into steam having the same temperature, a definite quantity of heat is required. Does anything of the kind occur when a gas expands? It is easily shown, even by so rough an experiment as Experiment I. that, when work is expended in compressing a gas, heat is produced, which, unless it is removed as fast as it is produced, will raise the temperature of the gas. Conversely, by such Experiments as II. and III., it may be shown that heat may be absorbed by a gas without the temperature being altered, provided the gas is allowed to expand and do work; but it is not so easy to decide whether the external work is the equivalent of the whole heat given, or whether it is the equivalent of a part of this heat only, the remaining part being required to produce the new state of the gas, namely, that of less density with the same temperature.

It has long since been remarked that when compressed air is allowed to escape it is cooled. But this we should expect if our theory of the equivalence of work and heat be true. Particles of matter which were at first moving at a certain rate have had their average velocity increased, and therefore kinetic energy has been produced. What has disappeared to account for its production? The experiment shows that heat has disappeared. How can we show whether all the heat which disappears as sensible heat is required to produce the kinetic energy of the moving molecules of gas? The natural answer is, destroy the motion, transform the kinetic energy into

heat, and compare the heat produced with that which at first disappeared.

This is exactly what is done in Experiments III. and IV. Gas rushes out of one receiver, and heat is taken from the gas which remains in this receiver. The kinetic energy of the gas is destroyed in a second receiver, and heat is produced. Now the heat lost and the heat produced are equal, so that on the whole there is no work done, no kinetic energy produced, and no heat lost. But the gas which was in the first receiver has expanded; hence it is evident that a gas does not require heat simply to enable it to occupy a larger space. A confirmation of this conclusion is afforded by Experiment V.; here the gas expands in such a manner that very little kinetic energy is produced, but actual work is done by the pressure, namely, the pushing back of the atmosphere, and the raising of water to a higher level. The work done and the heat lost by the gas are equivalent.

§ 45. **Distinction between internal and external energy.**—When heat is given to a body any of the following results may occur :—

(1.) The body may expand. In this case, if the pressure to which the surface is subjected be p units of pressure per unit of area, and v be the increase of volume, the work done in the expansion is represented by the product $p\,v$ (see § 2, p. 7).

(2.) The temperature may be raised.

(3.) The physical state of the body may be altered.

It is convenient to describe the first of these effects as external work, and the second and third as

internal work. Hence, when heat is communicated to a body it may be divided into two parts, one of which has for its equivalent the work done in driving back an external body pressing on the surface, as the atmosphere or a piston, and the other of which has for its equivalent the internal work. The latter may be again divided into two parts, one of which is required to raise the temperature of the body, and the other to change the physical state.

Now we know that if a body passes from one state to another in different ways, the external work may be different, and therefore the heat required to do this external work may vary, but we shall be able to show that the initial and final states, as regards volume and temperature, being the same, the internal work done is the same, however the change may be brought about.

The preceding experiments show that, for a permanent gas, the second of the two parts, into which the internal work or energy may be divided, is invariable and may be considered nought, so that the internal energy of a permanent gas depends only on the temperature.

§ 46. **Proposition.**—If from the equivalent of the whole heat, absorbed by a substance in undergoing a given change of state, the external work be subtracted, then the remainder is always the same in whatever way the change is produced.

Let the change from state A to state B be accompanied by the absorption of heat Q_1, and the production of work W_1.

Let the substance change back from B to A

giving up heat Q_2, and having work done on it represented by W_2, then the heat used is $Q_1 - Q_2$, and the work done is $W_1 - W_2$.

By the first law,

$$J(Q_1 - Q_2) = W_1 - W_2;$$

$$\text{or, } JQ_1 - W_1 = JQ_2 - W_2.$$

But Q_2 and W_2 are respectively the heat which would have been expended, and the work which would have been done, if the substance had changed from A to B by the second route reversed. Hence the proposition is proved.

The difference between the equivalent of the heat given and the external work done is what we have termed the internal work.

Hence the proposition may be stated in other words, by saying that, when a body changes from one given state to another, the internal work is the same, however the change may be produced, and it is equal to the difference between the equivalent of the heat supplied and the external work effected.

§ 47. **Proposition.**—To show that if a body passes from one given state to another in different ways the external work varies.

Let heat be given to the body, and, in consequence, let it expand. Let A and B represent the initial and final states; O *a*, *a* A (fig. 26, p. 83), representing the initial volume and pressure, and O *b*, *b* B, the final volume and pressure. Let the upper curve, A D B, represent the intermediate states as the body passes from the condition represented by

A to that represented by B. The work done in the expansion is represented by the area, *a* A D B *b*. Now let the body return to its initial condition, A, in a different way ; for instance, let heat be so taken away from the body that at any volume in the return the pressure is less than at the same volume in the departure from A, that is to say, let the temperature at any volume be less in the return than in the departure, then the pressure will be less, and the intermediate states between B and A will be represented by a curve, B E A, below A D B. The work done on the body to compress it to its original volume will be represented by the area, *a* A E B *b*. Hence less work will be done on the body in the compression than was done by the body in the expansion, and (assuming the equivalence of heat and work) less heat will be taken from the body during the compression than was given to it during the expansion. Let W_1 be the work done by the body, and W_2 that done on the body; let Q_1 be the heat absorbed by it, and Q_2 the heat rejected by it, and let $\mathcal{J}$ be the ratio of work to the heat which will produce it, then

$$W_1 - W_2 = \mathcal{J}(Q_1 - Q_2) = \text{area A D B E.}$$

CHAPTER X.

AIR-ENGINES.

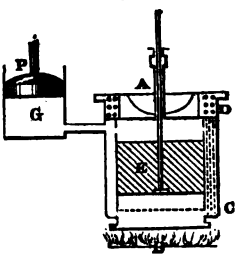
§ 48. **First Requisites for a Continuous Action.**—If a cylinder containing air be fitted with a loaded piston, and heat be applied to the cylinder, the air in expanding will raise the piston, and work will be done. Moreover the experiments of Chapter IX. show that air resembles very nearly a perfect gas, the internal work done in its expansion being very little; hence, if the gas be allowed to expand until its temperature is the same as before it received the heat, all the heat given to the air will be transformed into work. In order to use the air-cylinder and piston for the purposes of industry the action must be continuous; but, as the extent to which the expansion can be carried uninterruptedly is limited practically by the size of the cylinder, continuous action can only be got by repeating the expansion over and over again through the same range. For this purpose the piston must descend again, and, as the air below it opposes its motion, work must be done in the descent. Heat is produced as the air is compressed, and this heat must be withdrawn in order that the air may be restored to its initial state.

Hence in a complete cycle of operations of any air-engine capable of a continuous action, we must have a quantity, Q_2, of heat given to the air causing it to expand, a quantity of work, W_2, done by the air during expansion, a quantity of work, W_1, done upon the air during compression, and a quantity, Q_1, of heat withdrawn from the compressed air.

In order that the arrangement may be a useful one it is evident that W_1 must be less than W_2, and in the present chapter we shall show that, in this case, Q_1 will be less than Q_2. The ratio of $W_2 - W_1$ to $Q_2 - Q_1$ is the constant quantity, termed the dynamical equivalent of heat. The simplest form of air-engine is that invented by Stirling.

§ 49. **Description of Stirling's Air-Engine.**—This engine consists of two cylinders, which we will call respectively: the *working cylinder*, G, and *the receiver*, A B; with a tube, C D, termed the *regenerator*, which is packed either with wire gauze, perforated plates, or with thin, vertical, oblong strips of metal, with narrow passages between them.

FIG. 35.



The receiver has a double bottom, the inner one being pierced with small holes, and the space between the two being filled only with air. The piston, E, of the receiver is termed the plunger. It moves up and down within the receiver, fitting easily, so as to leave the least possible space without causing perceptible

friction. The plunger is hollow, and is filled with some substance of low conductivity.

Beneath the receiver is a fire which serves as the *source of heat.* The cooling is effected by the cold air on the outside of the surface, A, of the receiver, assisted by a current of water, which is forced by a pump through a coil of fine copper tubing surrounding the top, and shown at D in the figure. The outside air and this current of water together therefore constitute the *refrigerator.*

The regenerator, C D, connects the upper and lower parts of the receiver. When the engine has arrived at its state of uniform motion, and uniform expenditure of heat, the lower end, C, of the regenerator has nearly the higher temperature of the source, and the upper end, D, the lower temperature of the refrigerator. When the plunger descends, the hot air from below it passes through the regenerator (leaving its heat as it passes) to the upper part. When the plunger ascends, the cold air from above it is trans ferred through the regenerator to the space below. In the first case, the air at the higher temperature passing from the end B through the regenerator, cools as it goes, and arrives at the end, A, with the lower temperature, having left its excess of heat in the regenerator. When cold air afterwards passes in the opposite direction, its temperature rises, for it takes up the heat deposited in the regenerator, and enters the space at the end B with the higher temperature.

After the regenerator has become fully heated, therefore, this quantity of heat simply travels between it and the space B, and need not be drawn from the

furnace; but before this state is reached more heat will be left in the cells of the regenerator by the hot air from below than will be recovered by the cold air from above.

The plunger, E, and piston, P, are connected with the mechanism in such a way that they work alternately; the plunger being at the middle of its up-stroke when the piston, P, is at the beginning of its up- or forward-stroke, and being at the middle of its down-stroke when the piston, P, is at the beginning of its back-stroke.

The play of the machine, when the regenerator has become fully heated, is therefore as follows :—

1. The piston, P, being near its lowest position, the plunger rises, and air is transferred from above to below. This air does not change volume, but its temperature rises from the lower temperature, t_1, of the refrigerator to the higher temperature, t_2, of the source, and its pressure increases in consequence.

2. Having now access to the cylinder, G, this air, with its increased pressure, pushes up the piston, P, thereby doing work. Its volume therefore increases, but its temperature remains the same, for the tendency to cool in expanding is counteracted by the supply of heat from the furnace below, B, which is capable of maintaining a constant temperature in the base, B.

3. The plunger, E, now descends, and the air in the consequent transfer, without changing volume, changes temperature from t_2 to t_1.

4. Next, there being a free communication between the space below P and that above E, P descends, so that the air is compressed at the constant temperature, t_1,

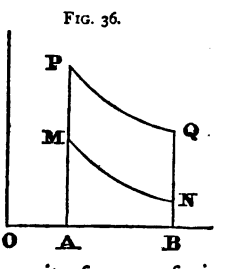
work being done in the compression, and the heat thus produced being carried off by the refrigerator.

A whole cycle has now been performed.

It is evident that, in an engine with a perfect regenerator, the air, when it arrives at the source or refrigerator, would already have the temperature, t_2 or t_1 respectively, of that part, and that the heat taken up or given out by the air would not alter its temperature.

§ 50. **Theory of Stirling's Air-Engine.**—A complete cycle may be divided into four parts. Of the three quantities—pressure, volume, and temperature—it will be seen that the first changes in each of these four parts, but that the volume and temperature are alternately variable and constant. First, the air is heated at constant volume, then it expands with constant temperature, next it is cooled to its original temperature at constant volume, and, finally, it is compressed to its initial volume, the temperature being constant. During the expansion, the temperature and therefore also the pressure, are higher than the temperature and pressure during compression; hence the work, W_2, done by the air during expansion, exceeds W_1, that done on it during compression, and the difference, $W_2 - W_1$, can be used, as we please, on external things. Let these changes be represented by a geometrical construction.

FIG. 36.



Let $OA = v_1$, the volume of a unit of mass of air at the initial temperature t_1.

Let A M $= p_1$, the initial pressure on a unit of area. While v_1 remains constant, the temperature changes to t_2, in consequence of the absorption of a quantity, Q, of heat. If N be the specific heat at constant volume, then (§ 42, pp. 94, 95)

$$Q = N(t_2 - t_1).$$

In this operation the pressure increases from p_1 (= A M) to p_2 (= A P), but as the volume remains the same no work is done. In order to keep the piston immovable it is of course necessary that the load on it should be increased from p_1 to p_2. In the next change the load of the piston is diminished, while the temperature remains constant, but the volume changes from v_1, represented by O A, to v_2, represented by O B. Since, during this change, v varies inversely as p, the arc, P Q, which expresses this variation, must be that of the equilateral hyperbola (§ 30). The area A P Q B represents the external work effected. Now, to prevent the air from cooling during the expansion, a quantity of heat, Q_2, must be communicated to it, the mechanical equivalent of which is the work represented by the area A B Q P. In the third stage of the cycle, the gas is reduced in temperature to t_1 without change of volume, and its pressure changes without expenditure of work from p_2, represented by B Q, to p_3, represented by B N, while the air gives up a quantity of heat equal to $N(t_2 - t_1)$, if we admit that N, the specific heat at constant volume, is independent of density. Finally, in the fourth and last period the air is compressed until its volume is again v_1, the temperature being kept at t_1. To effect this change

work has to be done on the air, and heat, Q_1, has to be subtracted. The work represented by the area, A M N B, is the equivalent of the heat Q_1.

In the first two periods of the cycle, the air receives heat, represented by $N(t_2-t_1)+Q_2$, and does work, represented by the area A P Q B. In the last two periods heat is taken away, equal to $N(t_2-t_1)+Q_1$, and work represented by the area, A M N B, is done upon the air. Hence the heat which has disappeared is equal to Q_2-Q_1, and the work effected is represented by the area M P Q N.

Now, there is a difference between the two parts, Q_1 and Q, or $N(t_2-t_1)$, into which the heat abstracted from the air has been divided, for the former cannot be used again in the same machine, but there are two conceivable ways in which the latter can be utilised. First, the heat rejected during the cooling in the third stage may be stored up and used to produce the heating in the first stage. For instance, it may be used to raise the temperature of a unit of mass of air, which can do work by its expansion at constant temperature, and, when the second mass cools in its turn, the heat which it gives out can raise the temperature of the first mass again between the same limits. By this arrangement the quantity $N(t_2-t_1)$ of heat is transferred backwards and forwards between two masses of air. To effect this passage is the purpose of the regenerator, mentioned in the general description of Stirling's engine. If the action of the regenerator could be made perfect, this part of the heat would not need to be drawn from the source after the first cycle.

The second conceivable way of using the heat referred to is by the insertion of an auxiliary heat-engine, receiving heat from the hot gas used in the primary engine after this gas has done its work. The whole work done would then be the sum of the separate amounts of work done by the two engines, and would exceed that of the primary engine, without requiring more heat to be taken from the source than is required for that engine.

The quantity of heat, Q, may therefore be utilised either in the same engine or in an auxiliary engine, between the limits of temperature used; it is not so, however, with the quantity, Q_1, which the air gives up when compressed at constant temperature. This is taken up by the refrigerator, and is there accumulated at a temperature t_1, and cannot therefore be used to raise the temperature of a body beyond t_1, nor even to maintain it at t_1 while it expands. It can be used in another machine where the highest temperature of the air or gas is not above t_1, but it is of no use to preserve the play of the original machine. This, then, is the quantity of heat which is necessarily given up by the machine, and the quantity which is transformed into work is $Q_2 - Q_1$.

§ 51. **Efficiency of an Engine.**—The ratio of the work done to the whole heat withdrawn from the source is termed the efficiency of the engine.

$$\text{Efficiency} = \frac{\text{work done}}{\text{heat expended}}.$$

Assuming the work equivalent of heat to be $\mathcal{J}$,

$$\text{Efficiency} = \frac{\mathcal{J}(Q_2 - Q_1)}{Q_2}.$$

Efficiency of a Stirling's Engine with a Perfect Regenerator.—Using the same letters and figure as in the preceding explanation, and applying the preceding definition, we see that

$$\text{The efficiency} = \frac{\mathcal{J}(Q_2 - Q_1)}{Q_2}.$$

Now Q_2 and Q_1 have for their respective equivalents the works represented by the areas, A B P Q and A B N M, in the figure (p. 109). Let these areas be divided into narrow strips by vertical lines, and let the heights of one of the strips up to M N and P Q respectively be p'_1 and p'_2, the heights of the first strip being, as before, p_1 and p_2. The equations to the curves, M N and P Q are respectively $p v = k t_1$ and $p v = k t_2$ (see p. 64). Since, for the same strip, the value of v is the same, and for the same curve, t_1 and t_2, are constant, it follows that the ratio—

$$\therefore \frac{p'_2}{p'_1} = \frac{p'_2 v}{p'_1 v} = \frac{k t_2}{k t_1} = \text{a constant},$$

and is therefore the same for all the strips. But for any strip

$$\frac{\text{Area to P Q}}{\text{area to M N}} = \frac{p'_2}{p'_1} = \frac{p_2}{p_1} = \frac{t_2}{t_1},$$

$$\therefore \frac{\text{Whole area, A Q P B}}{\text{whole area, A N M B}} = \frac{p_2}{p_1} = \frac{t_2}{t_1}$$

$$\therefore \frac{Q_2}{Q_1} = \frac{p_2}{p_1} = \frac{t_2}{t_1},$$

$$\therefore \frac{Q_2 - Q_1}{Q_2} = \frac{t_2 - t_1}{t_2}.$$

In other words, the fraction which expresses how much of the whole heat, taken from the source, is changed into work is the range of temperature divided by the higher temperature—all temperatures being measured from the absolute zero. The efficiency of the engine is proportional to the same fraction.

For example, if the temperature of the source is 146° C., and that of the refrigerator 34° C., the ratio of the heat utilised to the heat abstracted is

$$\frac{(146+273)-(34+273)}{146+273}=\frac{112}{419}.$$

Efficiency of a Stirling's Engine without Regenerator. —We have

Heat drawn from source $= Q_2+N(t_2-t_1)$,

Heat given to refrigerator $= Q_1+N(t_2-t_1)$,

Heat changed to work $= Q_2-Q_1$,

$$\therefore \text{The efficiency} = \frac{J(Q_2-Q_1)}{Q_2+N(t_2-t_1)}.$$

The work equivalent to (Q_2-Q_1) is represented by area (A Q P B—A N M B), or by

$$k\,t_2 \log_e r - k\,t_1 \log_e r,$$

if r stands for the ratio $v_2 \div v_1$ (p. 64). And the work equivalent to Q_1 is represented by A Q P B or $k\,t_2 \log_e r$. Hence the efficiency is proportional to

$$\frac{k\,(t_2-t_1)\log r}{k\,t_2 \log r+N(t_2-t_1)}.$$

This is evidently less than the efficiency of the engine with a perfect regenerator, for we may reduce it to the value already obtained for such an engine by

simply diminishing the denominator by the quantity $N(t_2-t_1)$.

Remarks on the Result.

(1.) On referring to § 40 (p. 88), the reason for the difference of efficiency when there is no regenerator will suggest itself, the reason being that, in certain parts of the cycle, the gas has *its temperature changed* while in contact with the heating and cooling bodies.

(2.) Without a regenerator the process is *not* reversible.

Commencing with the condition marked P (fig. 36), and proceeding backwards, we find:

i. The temperature of the air being reduced from t_2 to t_1 at constant volume, a quantity of heat, $N(t_2-t_1)$, is given to the refrigerator.

ii. The air expanding at constant temperature, t_1, does work, and withdraws Q_1 from the refrigerator.

iii. The temperature rising from t_1 to t_2 at constant volume, a quantity of heat, $N(t_2-t_1)$, is taken from the source.

iv. Being compressed to its first volume at constant temperature, t_2, the air receives work, and gives heat, Q_2, to the source. Hence the heat taken from the refrigerator is $Q_1-N(t_2-t_1)$, and that given to the source is $Q_2-N(t_2-t_1)$. But in the direct action without regenerator, $Q_2+N(t_2-t_1)$ is taken from the source, and $Q_1+N(t_2-t_1)$ is given to the refrigerator; hence, without a refrigerator, the cycle cannot be reversible.

(3.) The efficiency of the perfect form of engine is proportional to $\frac{T_2-T_1}{T_2}$ when temperatures are

measured from the point $-273°$ C. If temperatures be measured from 0° C., this expression becomes $\frac{t_2-t_1}{\frac{1}{a}+t_2}$. We have already seen (p. 62) that when the temperature, $-273°$ C., is made the zero of temperature, the laws which connect pressure, volume, and temperature of a gas are reduced to their simplest forms, and now we see that at the same time the efficiency of a gas-engine is also expressed in the simplest form.

We are now preparing the way for a more general view of heat-engines, and we shall find that by no possible arrangement can we obtain an efficiency greater than that obtained by the more perfect form of air-engine.

(4.) If the refrigerator of a gas-engine could be reduced to the absolute zero of temperature, the formula giving the ratio of the useful heat to the heat abstracted from the source would reduce to

$$\frac{Q_2-Q_1}{Q_2}=\frac{T_2-T_1}{T_2}=\frac{T_2}{T_2}=1,$$

$$\therefore Q_1=0.$$

That is to say, all the heat taken from the source would be used in doing the work, and none would be carried to the refrigerator. Neither could a body at this temperature be used as a source of heat, for in the equation $\frac{Q_1}{Q_2}=\frac{T_1}{T_2}$, if T_2, the temperature of the source, be zero, then must Q_2 also be zero. Such a body would therefore act as if absolutely devoid of

heat—for this reason, *the temperature* $\frac{1}{a}$ *degrees below* 0° *C., where* a *is the coefficient of expansion for a perfect gas, has been called the absolute zero of temperature.*

It has already been pointed out that heat is wasted when it passes between bodies at different temperatures without the agency of an intermediate body, and that this fact gives the condition of maximum efficiency. We will now state the condition in the form of a proposition.

§ 52. **Proposition.**—The condition of maximum efficiency in any engine is that the intermediate body, by whose change of volume work is effected, shall be at the same temperature as the source of heat when it receives heat, and at the same temperature as the refrigerator when it rejects heat.

First, let heat be received by the intermediate body at a temperature *below* that of the source; then an auxiliary engine may be used to transfer heat between these two bodies. This engine would require to abstract from the source, in addition to the heat transferred simply, the heat equivalent of the work done by it. It would therefore increase both numerator and denominator of the fraction which is proportional to the efficiency (see definition of efficiency, § 51, p. 112) by the same quantity, and would consequently increase the efficiency.

Secondly, let heat be rejected at a temperature *above* that of the refrigerator, then, evidently, an auxiliary engine may be introduced, to work between the body rejecting heat and the refrigerator, and this

would convert part of the heat rejected into work, without drawing more heat from the source. Hence it would increase the efficiency. Thus the efficiency cannot be a maximum when heat passes between two bodies at different temperatures without the agency of an intermediate body. Whenever, therefore, the working substance in an engine of maximum efficiency changes temperature, it must be without gain or loss of heat.

§ 53. **Reversible Processes.**—When heat is given to the gas in a cylinder fitted with a piston, if the temperature remains the same, the gas expands and does work; and if then the same amount of work be expended in compressing the gas, the same quantity of heat must be withdrawn in order that the temperature may remain unchanged. The operation is therefore a reversible one.

The series of operations which constitute a complete cycle in a heat-engine may be reversible. Suppose, for instance, that the engine takes from a hot body, or source of heat, a quantity of heat, S, and conveys to a cold body, or refrigerator, a quantity, R, doing external work, W, equal to $\mathcal{J}(S-R)$: then, if the expenditure of external work equal to W in moving the piston, and the withdrawal at the same time of an amount of heat, R, from the cold body are accompanied by the restoration to the source of the amount of heat, S, which left it, the series of processes is reversible.

Several remarkable and important properties are possessed by reversible or, as they are generally called, *perfect* engines.

§ 54. **Proposition. Carnot's Principle.**—With the same source and refrigerator no engine can have a greater efficiency than that of a reversible engine.

Let there be a reversible engine, E; let S be the heat drawn from the source, and R that given to the refrigerator when the work done is W.

Let there be also a second engine, E′, and to do the same work, W, let it take heat, S', from the source, and reject R'. Let the second engine be used to work the first engine, which is a reversible one, backwards.

Now the efficiencies of the two engines are respectively proportional to

$$\frac{W}{S} \text{ and } \frac{W}{S'}.$$

If possible, let the second of these fractions be greater than the first, then evidently S' must be less than S. But we may show that this is impossible: the heat taken from the source by the second engine is S', and that restored to it by the first is S; the heat carried to the refrigerator by the second is R', and that taken away from it by the first is R. The combined action of the two engines therefore takes from the source $S'-S$, and gives to the refrigerator the quantity $R'-R$. Since, on the whole, no work is done, $R'-R$ must be equal to $S'-S$. Hence, if S' be less than S, then R' will be less than R, or heat passes *from* the refrigerator *to* the source, that is to say, from the cold body to the hot one. This effect is produced without cost of work, for the combined engines require no power to work them—a result which is absurd, since it may be taken as an axiom

that—*Heat cannot be made to pass from a cold body to a hot one without the expenditure of work.*

Deductions:

(1.) By supposing E′ also reversible, we may invert the above reasoning, and prove that the efficiency of E cannot be greater than that of E′; hence, when both are reversible, their efficiencies are equal. Hence all reversible heat-engines, with the same source and refrigerator, have the same efficiency.

(2.) The maximum efficiency with source of heat at the absolute temperature T_2, and refrigerator at temperature T_1, is $(T_2 - T_1) \div T_2$.

(3.) The condition of maximum efficiency is that the series of processes which constitutes a complete cycle shall be *reversible*. The preceding investigations (§ 52) enable us to see that the same condition is expressed, in other words, by saying that the gas, or working substance, receives heat at the constant temperature of the source, and rejects heat at the constant temperature of the refrigerator, and neither receives nor rejects heat while at other temperatures.

CHAPTER XI.

RELATIONS BETWEEN THE SPECIFIC HEATS OF GASES.

In this Chapter we have to show how the three quantities M, K, and N, referred to in Chapter VIII., are related to one another and to J, the dynamical equivalent to heat. It will be seen that N can be calculated from the value of K given by direct experiments, by combining it with a result deduced from the experimental determination of the velocity of sound; and further that, when K and N are known, the value of J can be calculated from them with the help of known constants.

§ 55. **Equation involving M, K, and N.**—Suppose a gas to have its temperature increased by a small amount t', while the pressure remains constant, then Q', the quantity of heat per unit of mass absorbed by the gas, will be equal to Kt'. The volume of the gas will also be increased by a small quantity, v'. Now, it is evident that the final circumstances may be attained by two steps, the sum of the quantities of heat required for the two steps being the same as Q' above. For instance, we may suppose the temperature to increase by the amount t', while the volume remains constant, and then we may suppose the temperature constant while the volume changes

from v to $v+v'$. For the first change the heat required per unit of mass will be Nt', and for the second change, Mv'. Hence

$$Q' = Kt',$$
$$Q' = Mv' + Nt',$$
$$\therefore Kt' = Mv' + Nt'.$$

The values of K for air and other gases have been carefully determined by Regnault, according to the plan described in § 41, but there are great difficulties in the way of a direct determination of N.

§ 56. **Proposition.**—The specific heat with constant pressure is greater than the specific heat with constant volume, or the ratio $\frac{K}{N}$ is greater than unity.

Let the temperature of a mass of gas kept under constant pressure be raised from t to $t+t'$, and let the consequent increase of volume be from v to $v+v'$. Now imagine the gas compressed until it has its original volume, v. By this means the temperature will receive a second increase, t'', and the gas will be in the same condition as it would have been in if it had been heated without being allowed to expand; hence it is evident that the quantity of heat which raises the temperature t' with constant pressure, raises it $t'+t''$ with constant volume, and therefore, for a unit of mass, this quantity of heat is equal to either of the expressions

$$Kt' \text{ and } N(t'+t'')$$

$$\therefore K t = N(t + t'),$$

or
$$\frac{K}{N} = 1 + \frac{t'}{t},$$

Hence the proposition is proved.

Let $t = 1°$ C. : then, since a permanent gas expands by $\frac{1}{273}$ of its bulk at 0° C., if the temperature increases 1° C. with constan pressure, therefore t' *is the rise of temperature consequent on compressing a gas* $\frac{1}{273}$ *of its bulk at* 0°.

We will denote the ratio of the two specific heats by γ

$$\therefore \gamma = \frac{K}{N} = 1 + \frac{t'}{t},$$

where t and t' have the values described above.

It follows from the experiments of Dulong on the velocity of sound that γ is nearly the same for most of the permanent gases, and is independent of temperature and pressure, and as Regnault's experiments, already referred to, prove that K is independent of temperature and pressure, it follows that the same applies to N.

§ 57. **To Calculate the Value of γ from the Velocity of Sound.**—The investigation of the velocity of sound through the atmosphere or any gaseous medium is based on the following fundamental proposition of dynamics :—'The velocity of the pulses in an elastic medium is as the square root of the elasticity divided by the density of the medium, or $v = \sqrt{(e \div d)}$.' In the case of a gas at a constant temperature, e is measured by the pressure, and for unconfined air this is the atmospheric pressure.

Let g = acceleration due to gravity;

w = the weight of a unit of volume of air at the density d;

m = the weight of a unit of volume of mercury;

b = the height of the mercurial barometer.

Then evidently the atmospheric pressure $= e = b\,m$. And, as the density of a substance is the number of units of mass in a unit of volume,

$$\therefore d = \frac{w}{g};$$

substituting these values of e and d,

$$\therefore v = \sqrt{(g\,m\,b \div w)}.$$

This formula would represent the velocity of sound in air, if there were no change of temperature. But the rapidly alternating condensations and rarefactions, which constitute the vibrations of sound, cause respectively a rise and fall of temperature. Consequently, the increment of pressure in those portions of air which at any given instant are compressed, is greater than what corresponds to the mere increase of density; and, similarly, at those parts where there is a rarefaction, the decrement of pressure is greater than that which would be caused merely by the decrease of density. These effects are equivalent to an increase of elasticity, and Laplace showed that, in order to take account of them, the above value of v must be multiplied by $\sqrt{\gamma}$, that is to say, by the square root of the ratio of the two specific heats of air.

$$\therefore v = \sqrt{(g\,m\,b\,\gamma \div w)}.$$

Now, at the temperature of melting ice, and when

the height of the barometer is 2·494 feet, it is found by experiment that $v = 1089$ feet per second, the ratio $m \div w = 10466$, and $g = 32{\cdot}19$ feet per second,

$$\therefore \gamma = \frac{1089 \times 1089}{32{\cdot}19 \times 10466 \times 2{\cdot}494},$$
$$= 1{\cdot}411.$$

Since the specific heat at constant pressure, K, was found by Regnault's experiment to be ·2374, the above value of γ gives (§ 54)

$$N = {\cdot}2374 \div 1{\cdot}411 = {\cdot}168.$$

§ 58. **Proposition.**—To find an expression for the difference of the two specific heats in the case of the permanent gases.

Let K, N, and M be respectively the specific heat with constant pressure, the specific heat with constant volume, and the latent heat of dilatation.

Let a unit of mass of the gas be taken, and let the pressure have a constant value, p, but let the temperature be raised by the application of heat from t to $t + t'$ where t' is small. Let the consequent change of volume be from v to $v + v'$, and let Q' be the quantity of heat absorbed during the operation.

Then, by § 55,

$$Q' = Kt' = Mv' + Nt'.$$

But, by Gay-Lussac's law, if we measure temperatures from the absolute zero,

$$\frac{v + v'}{t + t'} = \frac{v}{t},$$
$$\therefore v' = \frac{vt'}{t}.$$

Substituting therefore in the above equation

$$K \cdot t' = \frac{M \cdot v \cdot t'}{t} + N \cdot t',$$

$$\therefore K - N = \frac{M \cdot v}{t} = \frac{M}{p} \cdot \frac{vp}{t},$$

$$= \frac{M \cdot R}{p},$$

if R denote the quotient $vp \div t$, which is constant for a given quantity of a given gas.

§ 59. **Proposition.**—To find the value of $\mathcal{J}$, the dynamical equivalent of heat, in terms of the two specific heats of a perfect gas.

Let a quantity, Q, of heat be given to the gas, and let it be divided into a large number of small parts, each equal to q': for each the following equation holds

$$q' = N \cdot t' + M \cdot v';$$

and therefore, for the whole quantity of heat, we have, since N is constant,—

$$Q = \Sigma q' = N \cdot \Sigma t' + \Sigma \cdot Mv'.$$

Now let the gas undergo a complete cycle of changes, so that it arrives at precisely the same state at the end of the cycle as at the beginning. Then $\Sigma t' = c$

$$\therefore Q = \Sigma \cdot M \cdot v',$$

and (§ 58)
$$M = \frac{K - N}{R} \cdot p,$$

$$\therefore Q = \frac{K - N}{R} \Sigma p v',$$

but $\Sigma p v' =$ the external work, W, done during the cycle,

$$\therefore Q = \frac{K-N}{R} \cdot W.$$

This shows that when the quantity of heat is used in a complete cycle of transformations, in which the temperature and molecular forces in the substances employed are exactly in the same condition at the beginning and the end of the cycle, so that the whole effect produced by the heat is the external work, then this external work is to the quantity of heat which produces it in the ratio

$$\frac{R}{K-N}$$

Let this ratio be denoted by the letter $\mathcal{J}$, then

$$\mathcal{J} = \frac{R}{K-N}$$

This expression gives a new value of $\mathcal{J}$, and its coincidence with the values determined by other methods forms a forcible argument in favour of the Mechanical Theory of Heat.

We do not know the constants R, N, and K for a perfect gas, but we know them for air, which we have already found to differ but little from a perfect gas. Thus $K = \cdot 2374$, and $N = \cdot 168$, while R $(= vp \div t)$ may be found as follows:

A pound of air forced into a cubic foot of space, and reduced to a temperature of 32° F., exerts a pressure per square foot of 26,300 lbs., and the absolute temperature corresponding to 32° F., if we use degrees Fahrenheit, is 490·9, therefore

$$R = \frac{26300 \times 1}{490{\cdot}9} = 53{\cdot}57,$$

and consequently,

$$\mathcal{J} = \frac{R}{K-N} = \frac{53{\cdot}57}{{\cdot}0694} = 772.$$

If we use units in the metric system, we may proceed thus: A cubic metre of air at 0° C. under the normal pressure of 760 mm. was found by Regnault to weigh 1·2932 kilog.; hence one kilogramme of air has a volume of $1 \div 1{\cdot}2932$, or ·77328 cubic metre. The pressure of 760 mm. on a square metre is 10333 kilog.

$$\therefore R = \frac{p v}{t} = \frac{10333 \times {\cdot}77328}{273} = 29{\cdot}269,$$

$$\therefore \mathcal{J} = \frac{R}{K-N} = \frac{29{\cdot}269}{{\cdot}0694} = 423 \text{ nearly.}$$

If we use centimetres and grammes as units, the numerical value of $\mathcal{J}$ becomes 42,300.

§ 60. **Internal Energy.**—If a quantity of heat, Q, be given to a substance, part will be expended in doing external work, part in raising the temperature, and part in producing a new state. The first we have called the external work, the last two together the internal energy.

Proposition.—The internal energy of a gas depends only on the temperature.

Let a quantity of heat, Q, given to a gas produce a change of internal energy, I, and the performance of external work, W, then

$$\mathcal{J}\, Q = I + W,$$

but (§ 59) $Q = Nt + \Sigma M v'$ and $M = \frac{K-N}{R} p = \frac{p}{\mathcal{J}}$,

$$\mathcal{J} Q = \mathcal{J} N t + \Sigma p v' = \mathcal{J} N t + W,$$

$$\therefore I = \mathcal{J} N t.$$

Therefore, since experiment shows that N is constant for all temperatures, the internal energy varies as the temperature. Hence the heat expended in internal work when any change of state is produced in a perfect gas is simply $N(t_2-t_1)$, where t_1 and t_2 are the temperatures at the beginning and end of the change, and N is the specific heat with constant volume.

§ 61. **Proposition.**—When a perfect gas expands without gain or loss of heat, the pressure and volume are connected by the equation,

$$p v^{\gamma} = \text{a constant},$$

where γ is the ratio of the two specific heats.

The above conditions would be secured if the gas were contained in a vessel impervious to heat, or if the expansion were so sudden as not to allow time for the communication of heat between the gas and the vessel containing it.

Suppose a unit of mass of the gas to experience a small change of volume from v to $v+v'$, and a small change of temperature from t to $t+t'$ without any interchange of heat between it and surrounding objects.

Then the following equations hold (see § 55, p. 122, and § 58, p. 126),

$$M v' + N t' = 0,$$

$$M = (K-N)\frac{t}{v}.$$

Eliminating M, and substituting γ for the ratio $\frac{K}{N}$,

$$(\gamma-1)\frac{v'}{v} + \frac{t'}{t} = 0.$$

If the whole change from volume v_1 to v_2, and temperature t_1 to t_2, be divided into small changes, an equation, like the above, may be formed for each, and the sum of the whole determined (see § 30, p. 65).

The sum of the terms $\frac{v'}{v}$ will be $\log \frac{v_1}{v_2}$.

The sum of the terms $\frac{t'}{t}$ will be $\log \frac{t_1}{t_2}$.

Hence if we suppose γ the same for all temperatures,

$$(\gamma - 1) \log \frac{v_1}{v_2} = -\log \frac{t_1}{t_2},$$

$$\therefore \left(\frac{v_1}{v_2}\right)^{\gamma-1} = \frac{t_2}{t_1},$$

but $$\frac{p_1 v_1}{p_2 v_2} = \frac{t_1}{t_2};$$

by multiplication, $$\therefore p_1 v_1^{\gamma} = p_2 v_2^{\gamma},$$

or $p v^{\gamma}$ is constant.

§ 62. **Adiabatic Lines.**—If a substance can expand without gain or loss of heat, and a curve is drawn, such that the abscissa and ordinate of any point respectively represent the volume of a unit of mass, and the corresponding pressure per unit of area, this curve is termed an adiabatic line.

Imagine, for example, that a pound of the substance is confined in a cylinder closed by a piston, both being impervious to heat. Let the

piston be a square foot in area ; let p be the load on the piston, and v its height above the base of the cylinder. Set off an abscissa, O A, equal to v, and an ordinate A P equal to p. If the load be diminished v will increase, and the point, P, in the diagram will trace out an adiabatic line.

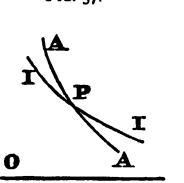
Adiabatic Lines for Perfect Gases.—The preceding proposition shows that the equation to an adiabatic line for a perfect gas, and approximately for a permanent gas, is

$$p\,v^{\gamma} = \text{a constant, } a.$$

This constant will vary with the quantity of heat contained in the substance when it is placed in the impervious cylinder. By beginning with a given quantity of heat, and adding successively one unit of heat at a time, a series of adiabatic lines may be drawn, corresponding to equal differences in the quantity of heat contained in the gas.

It is easily seen that where an adiabatic line and an isothermal line on such a diagram intersect, the former is inclined at a greater angle to the horizontal axis than the latter.

FIG. 37.



Let the equation to the isothermal line, I I, be $p\,v = i$, and that to the adiabatic line, A A, be $p\,v^{\gamma} = a$, and let them intersect in P (fig. 37). Then for the point P, p and v have the same values for both curves, which we may denote by p_0, v_0

$$\therefore \text{ for the isothermal, } p\,v = p_0\,v_0,$$

$$\text{and for the adiabatic, } p\,v^{\gamma} = p_0\,v_0^{\gamma}.$$

Now let v be an abscissa, a little greater than v_0; suppose, for instance, that $v = m v_0$, where m is a number a little greater than unity, and let the ordinates in the two curves corresponding to the abscissa, v, be respectively i and a.

Then
$$i v = p_0 v_0 \quad \therefore m i = p_0,$$
$$a v^\gamma = p_0 v_0^\gamma \quad \therefore m^\gamma a = p_0,$$
$$\therefore i = m^{\gamma-1} a,$$

since $(\gamma - 1)$ is positive, $m^{\gamma-1}$ is greater than unity,

$$\therefore i \text{ is greater than } a.$$

On the contrary, if v be a little less than v_0, so that m will be less than unity, then will i be less than a. Hence the curves cross at P, and the adiabatic curve is inclined at the greater angle to the axis of volumes.

CHAPTER XII.

GENERAL THEORY OF HEAT-ENGINES.

In Chapters VIII. and IX. the action of engines which are in actual use was described; we have now to consider the theory of heat-engines in its most general form. We begin by investigating a complete cycle of operations of an imaginary engine conceived first by Carnot, and generally termed Carnot's Reversible Engine.

In such a cycle the working substance returns precisely to its original condition, and we are therefore sure that no work has been required to produce change of state; in other words, there is no change of the internal energy of the substance.

The theory of this ideal engine leads to very important general conclusions, and, in particular, affords a strictly scientific and exact definition of equal differences of temperature.

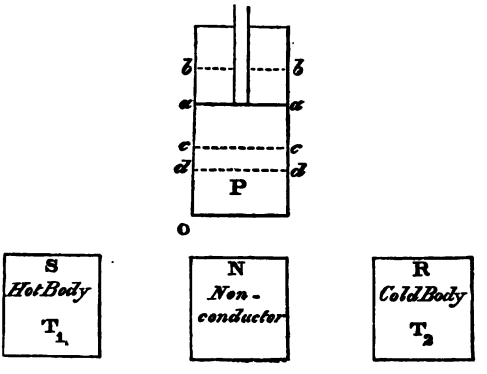
§ 63. **Description of Carnot's Reversible Engine.**—Let the sides of the cylinder and the piston be perfect non-conductors of heat, and let the bottom be a perfect conductor, so that all heat entering or leaving the cylinder passes through the bottom.

Let S and R be two bodies which can be kept always at the constant temperatures T_1, and T_2, respectively absolute scale), and let each of them be capable of communicating to, or abstracting from, any third body

placed in contact with it an indefinite amount of heat, so as always to change the temperature of this body to T_1 or T_2, as the case may be. Let N be a stand which is a perfect non-conductor of heat, and let P be the working substance.

It will be convenient for the purposes of reasoning to let the working substance in the beginning have the higher temperature, T_1, of the body S, the piston then

FIG. 38.



occupying the position marked *a–a*, and then let a complete cycle of operations occur as follows :—

First. Let the cylinder be placed on the stand N, and let the load on the piston be diminished so as to allow it to rise gradually. As no heat can get to the working substance, P, its temperature will fall. Let the operation continue until the temperature falls from T_1, that of S, to T_2, the temperature of R, and then let the position of the piston be that marked *b–b*.

Second. Now let the cylinder be transferred to R ;

there is of course no passage of heat. Force down the piston to a position *c–c*, then work will be done on the contents of the cylinder, and the immediate effect will be to raise the temperature, but heat will instantly flow into the body R, so that the temperature will remain at T_2.

Third. Let the cylinder be next carried to N, and let the piston be pressed in still further to the position *d–d*. As in this case no heat can pass from the cylinder the temperature will rise. Let the process be continued until the substance, P, assumes its original temperature T_1.

Fourth. Now let the cylinder be placed on S. There is at first no passage of heat, but let the piston rise to its original position *a–a*. Work will be done by the pressure of the substance P; heat will pass to the substance from S; and finally, as this substance will then have its original temperature and volume, it will exert its original pressure.

The result of the whole cycle of operations is, therefore, that:

(1.) A quantity of heat, Q_2, is given to a cold body.

(2.) A quantity of heat, Q_1, is received from a hot body.

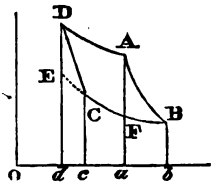
(3.) Work is done, by the substance while it is expanding, and upon the substance during the compression.

(4.) The working substance is left in exactly the same state as at first.

§ 64. **Graphical representation of the work done in a complete cycle by Carnot's engine.**—Let us suppose the area of the base of the piston unity, then

the volumes v_a, v_b, v_c, v_d, successively occupied by the working substance will be equal respectively to the lengths o*a*, o*b*, o*c*, o*d* (fig. 38). Let abscissæ be measured off equal to these lengths, and let ordinates be drawn at the points *a*, *b*, *c*, *d*, (fig. 39) proportional to the pressures p_a, p_b, p_c, p_d, exerted by the working substance on the piston in its four positions respectively. Let these ordinates be *a* A, *b* B, *c* C, *d* D, and join the points A, B, C, D by curves whose abscissæ represent the volumes successively assumed by the substance during the cycle, while the ordinates represent the corresponding pressures.

FIG. 39.



Thus B C and D A, the lines traced during the second and fourth operations, in which the substance changes volume at constant temperature, are isothermal lines; and A B and C D, the lines traced during the first and third operations, in which the substance changes volume while no heat enters or leaves it, are adiabatic lines.

The amounts of work done in the four operations are then represented respectively as follows:

First. Work done *by* substance = *a* A B *b*.
Second. Work done *on* substance = *b* B C *c*.
Third. Work done *on* substance = *c* C D *d*.
Fourth. Work done *by* substance = *d* D A *a*.

Taking the first and fourth as positive, the second and third as negative, and adding, we have therefore:

Total work done in the whole cycle = A B C D.

The above reasoning shows that—

During the ascent of the piston more work is done against external forces than is required to be done by external forces during the descent to restore the piston to its first position.

Let the changes be so small that we may consider the figure, A B C D, a parallelogram.

Then $a\,d$ and $b\,c$ each represent the change of volume while the substance was expanding or contracting at constant temperature.

Let this small change of volume be denoted by v', then if M be the latent heat of dilatation, the quantity of heat taken from the source is represented by $M\,v'$ per unit of mass (see p. 94).

Produce B C to meet D d in E, and let A a meet B C in F. Then D E or A F, will represent the difference of the pressures which the working substance would exert at the temperatures T_1 and T_2, the volume being the same; for the line B C was obtained by the contraction of the volume at the fixed temperature T_2, and if the operation had been stopped when the volume was equal to O a, the original volume, then a F would have represented the pressure. Hence A F represents the difference p' of the pressures at the two temperatures T_1, and T_2, with the same volume.

The area of the parallelogram A B C D is equal to the area of the parallelogram A F E D on the same base, A D, and having the same height, and the latter area is D E $\times\, da$, that is $p'\,v'$. Hence the area, A B C D, is equal to $p'\,v'$.

§ 65. **Carnot's Function.**—Since Carnot's engine is reversible, whatever may be the working substance, if the limits of temperature remain the same the ratio

of the work done to the dynamical equivalent of the heat drawn from the source is constant. But the work done is represented by the area A B C D, or $p' v'$, and the heat withdrawn is Mv'. Therefore the ratio $p' \div \mathcal{J} M$, is constant for the same limits of temperature, and can therefore depend only on these limits. Let the higher temperature be t, and the lower $t - t'$, t' being in the present case very small. Then the above ratio is equal to some expression, which changes only when t and t' change. Let this expression be indicated by the product $t' C$.

$$\therefore \frac{p'}{\mathcal{J} M} = t' C.$$

Then C is a quantity which changes only when the limits of temperature change. It is termed Carnot's Function. Hence, in a complete cycle of Carnot's engine of small range, the ratio of the work done to the dynamical equivalent of the heat taken from the source is equal to the range of temperature, multiplied by a function of the temperatures, termed Carnot's Function. Now, by considering one case, namely, that of the air-engine, we have found that the above ratio is equal to the range of temperature divided by the absolute temperature of the source $(t' + t)$. The reasoning (see p. 113) which was applied to the figure on p. 109 may be applied in fact to the similar area, D E F A, in the preceding figure, the working substance being a perfect gas, of which D A and E F are isothermal lines.

But since the ratio is constant for the same temperatures, one case is sufficient to determine all.

$$\therefore \frac{p'}{\mathcal{J} M} = \frac{t'}{t}$$

Hence, Carnot's Function is the reciprocal of the absolute temperature of the source.

If the work done is W, and the heat taken from the source q, then :

$$\frac{W}{\mathcal{F}q} = \frac{t}{t'}, \text{ or } W = \frac{\mathcal{F}qt}{t'}.$$

§ 66. **A reversible engine of finite range may be considered equivalent to a large number of Carnot's engines of small range.**

Let q and $q-q'$ be the quantities of heat, respectively, taken from the source and given to the refrigerator by an engine of small range, working between temperatures t and $t-t'$, where t' is small.

Since the quantity of heat which disappears is q', the work done is $\mathcal{F}q'$.

But since a quantity, q, is taken from the source, the work is also represented by $\frac{\mathcal{F}qt}{t}$.

$$\therefore \mathcal{F}q' = \frac{\mathcal{F}qt}{t}.$$

$$\therefore \frac{q'}{q} = \frac{t'}{t}$$

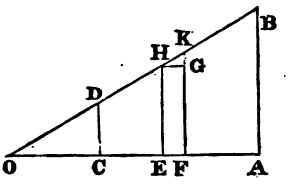
Imagine the engine whose range is finite made up of a great number of engines, with very small ranges, such that the refrigerator of any one is the source of heat for the next below it.

In any one of these engines if q be the heat taken in at temperature t, and $q-q'$ that given out at temperature $t-t'$, then :

$$\frac{q}{t'} = \frac{q}{t}.$$

Now let a figure be drawn in which the abscissæ from a fixed point, O, represent temperatures, and the ordinates quantities of heat received at the different temperatures (fig. 40). The line joining the extremities of these ordinates will be a straight line; for take O F, O E, to indicate the temperatures between which a small engine works, F K being q, E H being $q-q'$, and therefore K G being q', and E F or H G being t'. Then since

FIG. 40.



$$\frac{q'}{t'}=\frac{q}{t} \qquad \therefore \qquad \frac{\text{K G}}{\text{G H}}=\frac{\text{K F}}{\text{F O}}.$$

And this equation shows that K, H, and O lie on the same straight line.

Let us now imagine the temperature T_1 of the source of heat to be divided into n equal parts, and at the points in the line O A, which represent this division, let vertical lines be drawn to the line O B.

Imagine a number of reversible engines working through these intervals of temperature, each receiving the heat rejected by the one before it. Thus, if E F represents one interval of temperature, the corresponding engine will take in heat represented by F K, and reject heat represented by E H, turning the difference, which is represented by K G, into work. Since the intervals of temperature are equal, this difference will be the same for all the engines, and, if Q_1 be represented

by $A\,B$, the quantity of heat converted into work by each engine will be $\frac{Q_1}{n}$.

Hence, *if the temperature of a source of heat be divided into any number of equal parts, then the effect of each of these parts in causing work to be performed is the same.*

§ 67. **Remarks on the Second Law of Thermodynamics. Recapitulation.**—In examining the efficiency of heat-engines, we assumed as an axiom the following statement :—

(1.) Heat cannot be made to pass from a cold body to a hot one without the expenditure of work.

This axiom, which may be regarded as the Second Law of Thermodynamics, was stated by Sir W. Thomson in the following words :—

'It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of surrounding objects.'

By assuming this axiom we were able to prove Carnot's principle, namely, that :—

(2.) The efficiency of every reversible heat-engine is greater than the efficiency of any other heat-engine working between the same limits of temperature.

This proposition is enunciated by Sir W. Thomson as follows :—

'If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motion are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.'

It may be convenient for readers of this subject to remark, that some writers call Carnot's principle the Second Law, while Rankine states the result which we have deduced from Carnot's principle, in the preceding section (§ 66), as the Second Law.

The Second Law has enabled us to find an expression for the efficiency of a perfect engine, which is represented by the preceding figure. For let A B represent Q_1, the quantity of heat taken from the source of the great engine, and O A, the temperature, T_1, of the source. Let C D represent Q_2, the heat given to the refrigerator at temperature, T_2, represented by O C. Then since

$$\frac{AB}{OA} = \frac{CD}{OC} \quad \therefore \frac{Q_1}{T_1} = \frac{Q_2}{T_2},$$

or

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

Hence the efficiency of any perfect heat-engine varies directly as the range of temperatures, and inversely as the temperature of the source. This result has been established previously in §§ 49–52, where, after showing that it holds for a perfect gas-engine, we proved that if it is true for one reversible engine it must be true for any other. We now see that it follows from the theory of Carnot's Reversible Engine applied to any working substance whatever, provided we use the known laws of gases to determine the form of Carnot's Function.

Since, if W be the work done in the time during which the heat, Q_1, leaves the source,

$$\frac{\mathcal{J}(Q_1-Q_2)}{\mathcal{J}Q_1}=\frac{W}{\mathcal{J}Q_1}=\frac{T_1-T_2}{T_1},$$

or
$$W=\frac{\mathcal{J}Q_1(T_1-T_2)}{T_1}.$$

§ 68. **The Absolute Scale of Temperatures.**—The equation,

$$\frac{Q_1}{T_1}=\frac{Q_2}{T_2},$$

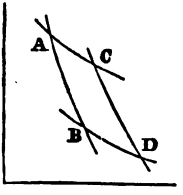
shows that, if two bodies maintained at different temperatures are respectively source and refrigerator of a perfect engine, then their absolute temperatures are to one another as the quantities of heat taken in and rejected respectively, or 'The temperatures of two bodies are proportional to the quantities of heat respectively taken in and given out in localities at the one temperature and at the other respectively, by a material system subjected to a complete cycle of perfectly reversible thermodynamic operations, and not allowed to part with or take in heat at any other temperature.'

This law affords another mode of measuring intervals of temperature. We have already seen that thermometers made of different substances differ in their indications of temperature, if graduated in the same way. But here we have a physical effect due to difference of temperature, which is independent of the nature of the operating body, namely, the power which bodies possess in consequence of difference of temperature of turning heat into work. When perfect engines receive quantities of heat proportional to the temperatures of the bodies which serve them as sources of heat, *equal intervals of temperature are the*

ranges of those engines which convert equal amounts of heat into work. The preceding investigations show that the scale of temperatures formed according to this definition, would coincide with the scale furnished by a perfect gas-thermometer, and there would not be any *appreciable* difference between this scale and that of the air-thermometer.

This is what we have already termed the *absolute* scale of temperatures. It does not depend on one particular substance, but depends on a common property of all substances. It is true that to construct the scale a more elaborate process is required than that used with ordinary thermometers, but it leads to really definite results. The degree centigrade may be thus described according to this plan. Take any substance and construct on a plan any two adiabatic lines, A B, C D, differing by the absorption of any unit of heat. Construct the isothermals, B D, A C, corresponding respectively to the temperatures of melting ice and saturated steam under a pressure of 760 mm. of mercury at 0°, and in a given latitude (45°). Drawing ninety-nine isothermals between A C and B D, such that the areas contained between every consecutive pair of isothermals, and the lines, A B, C D, are equal, then the interval of temperature corresponding to two consecutive isothermals is the 'degree centigrade.' The experiments of Joule and Thomson show that the temperature of melting ice is nearly 274 of these degrees above the absolute zero of temperature.

FIG. 41.



CHAPTER XIII.

THEORY OF MOLECULAR MOTION.

In this last chapter we again encounter the question, What is heat? and show that something more may be asserted than that heat may be produced from and converted into energy. There is at least a very high degree of probability that heat is simply kinetic energy. The phenomena connected with radiation, and particularly the identity between the laws of light and those of radiant heat, suggest that the molecules of a hot body are in a state of agitation. The phenomena of diffusion furnish evidence that the molecules of gases and liquids do not simply oscillate about a mean position, but make extensive excursions. Starting from these points, and being guided by the known properties of bodies, we are able to form a theory which is not contradicted by any facts, and which points out the directions in which new discoveries may be made.

§ 69. **Experiments. Ninth Series.** *To show that Radiant Heat is subject to laws in every way similar to the laws of light.*—I. If a heated body—a kettle of boiling water, for example—is suspended in a room, it is found that heat leaves it in all directions. A delicate thermometer placed on any side will indicate a higher temperature after the introduction of the hot body than before. At the same time the body cools. Heat which emanates from a hot body

in this way is termed Radiant Heat. It passes from its source equally on all sides in straight lines; it travels in vacuo as well as in air; it traverses the distance between the sun and the earth along with light, and there is no reason to think it has a velocity different from that of light.

II. Like light, radiant heat passes freely through some bodies, but not through others—although the bodies which are transparent to light are not necessarily transparent for all kinds of radiant heat. A beam of the sun's rays will pass through a plate of rock-salt without its heating effect being sensibly diminished. Water intercepts much of the heat but allows a great part of the light to pass. Bisulphide of carbon is transparent with regard both to light and to radiant heat, but when iodine is dissolved in it, the solution is opaque to light but transparent with regard to radiant heat. Most gases are transparent to light, but they have very different actions as regards heat. Ammonia intercepts 1200 times as much of the heat in a beam of solar rays as an equal column of air under the same pressure, and thirty times as much as a similar column of chlorine.

III. The colours of objects are accounted for by supposing that, when the sun's light falls on them, they abstract from it certain parts, differing according to the nature of their substance, and send back the rest. A body which is perfectly black absorbs all the light which falls on it; a body which is white absorbs little or none. Now a body may at a given temperature radiate more light than it absorbs, so that on the whole there is an emission of light; or, if a stronger

light fall on it at this same temperature, it may absorb more than it radiates, so that on the whole there is an absorption of light. Now it is found that the light which a body gives out is exactly of the same colour as that which it absorbs at the same temperature. Pieces of iron and white earthenware will serve as examples. The first absorbs nearly all the light falling on it, the second reflects nearly all. When both are placed in a clear and bright fire, the iron glows and gives out a bright light, while the earthenware appears dull by comparison. If red glass be placed in a beam of white light, only the red light of the beam passes through it; and if a second plate of red glass be placed in the course of this red light, the glass will have little effect, whereas a plate of glass of a pure green colour will intercept the beam entirely. Similar facts are found to exist in connection with radiant heat. Radiant heat from different sources is intercepted in different degrees by the same body. If a beam of radiant heat from a lamp, the light of which has been intercepted by a screen formed of a solution of iodine in bisulphide of carbon, falls on a plate of rock-salt, about 8 per cent. is intercepted, but a very much smaller proportion of the remainder is afterwards intercepted if a second plate of rock-salt is introduced into the beam. If the first plate of rock-salt is heated so as to become a source of radiant heat, then nearly the whole of a beam of this heat is stopped by a second and cool plate of rock-salt. A first plate of alum, 0·1 inch thick, allows only 9 per cent. of the radiation from a naked oil flame to pass through it, but of this amount a second plate of alum passes fully

90 per cent. We see therefore that it is equally true of heat and light, that *if a body, under one set of conditions, absorbs more rays than it gives out, and, under another set of circumstances, radiates more than it absorbs, the excess of absorption, or the excess of radiation respectively, affects the same kind of rays in both cases.*

IV. Radiant heat may suffer reflection, refraction, polarisation, and interference.

(*a.*) Radiant heat is reflected from a bright metal surface, the laws of reflection being identical with those of light. Thus if a cylindrical beam of dark radiant heat fall on a concave mirror, it will be reflected to the same focus as a similar beam of light.

(*b.*) Heat emanating from a non-luminous source may be refracted, and when this is the case, the laws of refraction for heat are identical with the corresponding laws for light. Thus a rock-salt lens will bring a conical beam of dark radiant heat to a focus so as to ignite combustible materials placed there. A prism of rock-salt or bisulphide of carbon will deflect a beam of dark heat and disperse it so as to form a lengthened spectrum, resembling the spectrum of light.

(*c.*) The wave-theory of light led to the discovery of the phenomena of interference. The two readiest ways of producing the phenomena are, first, by causing light from a narrow slit to be reflected at the surface of two small mirrors, very nearly but not quite in the same plane (Fresnel's interference mirrors); and secondly, by passing the light from the slit through a glass prism (Pouillet's prism), the obtuse angle of which is nearly 180°. Though Melloni, who investigated the properties of radiant heat, detected polarisation, he failed to discover interference; but the

phenomenon has been demonstrated by both the instruments just mentioned.

Fizeau and Foucault were the first to observe the phenomenon of the interference of heat rays. They employed, in connection with Fresnel's interference mirrors, a spirit thermometer with a cylindrical bulb of very small diameter. On gradually moving this instrument in a plane stretching across the middle of the field, the experimenters found the successive readings to proceed by regular alternations, ascending and then descending, the highest reading corresponding to the middle of the central luminous band.

The same phenomenon was subsequently observed by Knoblauch, who used a Pouillet interference-prism and a linear thermo-electric pile.

(*d.*) The polarisation of heat by reflection from the surface of glass was clearly demonstrated by Bérard in 1812. When heat was reflected by two glass mirrors in succession, he found that the beam reflected by the second mirror was considerably more intense when the planes of reflection of the two mirrors coincided than when they were at right angles to each other. But it is principally by the labours of various subsequent investigators that the phenomena of the polarisation of heat have been clearly demonstrated. Knoblauch discovered that in radiant heat, as in light, the polarisation produced by reflection is most complete when the rays are incident at some particular angle depending on the nature of the reflecting substance. De la Provostaye and Desains proved not only that the polarisation of heat takes place under the same conditions as the polarisation of light, but also that the properties of polarised heat agree pre-

cisely with those of polarised light. For instance, they calculated the intensity of a reflected beam, for various angles of incidence, from formulæ established for light, and found the results to agree precisely with those furnished by direct experiments with polarised heat. Again they proved that a powerful magnet produces a rotation of the plane of polarisation of heat, as it does in the case of light.

V. *Experiment showing the Diffusion of Gases.*—Let two jars be filled with different gases as, for example, oxygen and hydrogen, and let them be connected by a long glass tube passing through perforated corks, the jar of hydrogen being placed uppermost. In the course of a few hours oxygen will ascend to the upper jar, and hydrogen will descend to the lower. Ultimately both jars will contain a mixture of the two gases in the same proportion, and this will continue uniform and permanent. Similar results occur with any other gases or vapours which do not act chemically on one another.

Again let a membrane be tied over the mouth of a glass vessel which is filled with oxygen gas, and let the vessel be placed under a bell-jar of hydrogen. The gases will diffuse through the porous membrane, but the hydrogen will pass inwards more rapidly than the oxygen passes outwards, and consequently, after an hour or two, the membrane will be distended outwards. If the small vessel be filled with hydrogen and the bell-jar with oxygen, the membrane will become concave instead of convex, showing that more hydrogen than oxygen has passed through the membrane.

By making the smaller vessel a graduated tube

closed at one end by a plug of plaster of Paris, the open end being placed under mercury, the rates of diffusion may be measured. It is found that the rates of diffusion of two gases are inversely proportional to the square-roots of their densities. For instance, the densities of hydrogen and oxygen being as 1 to 16, and the square-roots of the densities therefore as 1 to 4, the volumes of hydrogen and oxygen which diffuse in a given time through the separating porous plug are as 4 to 1. When a mixture of gases is introduced into the diffusion tube, each preserves the rate of diffusion peculiar to itself, so that a partial mechanical separation of two gases of different densities may be effected by diffusion.

§ 70. **Remarks on the Experiments.**—What is usually called the Undulatory Theory of Light may now be said to have passed from the rank of a mere theory, and may be looked upon as an established fact. We may now take it for granted that a subtle elastic medium pervades space, and that light consists of waves formed by the oscillations of the particles of this medium.

The identity of the laws of light and of radiant heat show that the same arguments which establish the undulatory theory for the first, may be used to prove a similar theory for the second. We may, therefore, account for radiation as follows :—When a hot body is allowed to become a source of radiant heat, waves are produced all around it in the ethereal medium which is the means of transmitting light. In proportion as these waves are produced, the body cools. If the waves fall on a cold body which neither reflects

nor transmits them, they are destroyed, and the temperature of the body rises.

During the interval between the instant at which the heat leaves the hot body, and the instant at which it reaches the cold body, it exists in the intervening space as the energy of moving particles, that is to say, as kinetic energy. It is natural to suppose that when the waves are produced, and when they disappear, there is not a production and disappearance of kinetic energy from and into something different, but that the energy is preserved all through, the changes consisting only in its transmission from one set of particles to another. To produce the waves the outer surface of the hot body must be in a state of motion, and when they disappear, an equivalent kinetic energy must be developed in the body which is heated. The propagation of heat is therefore analogous to that of sound. The vibrations of the stretched string of a piano produce waves in the air, and at the same time the vibrations of the string subside. If the waves fall on another string or other body capable by its vibrations of producing waves of the same length, this body is put in motion, and the waves are in consequence weakened, but if they fall on a body whose time of vibration does not correspond, the body does not take up the motion, but reflects the waves with but little loss. By the theory before us, the radiation and absorption of sound are made analogous to the radiation and absorption of heat. It is true we do not detect any motion of the hot body as a whole or of the parts with relation to one another. We do not alter the character of the heat radiated by dividing the body into parts, as we

alter the character of the sound by dividing the string. If heat is energy of motion, it must be motion of portions of the body so small that it is beyond the power of the senses to distinguish them.

We will now show that by supposing the motion to be that of particles too small to be separated, we may account for all the laws and phenomena which we have investigated. It is highly probable, therefore, that not only are heat and work mutually convertible, but to convert one into the other is simply to transfer kinetic energy from one set of particles to another.

The plan according to which we proceed is as follows :—

(1.) We assume an undulatory theory of Radiant Heat, and account for radiation by supposing that heat exists in a body by virtue of the motion of the small particles or molecules of which it is composed.

(2.) We examine what must be the nature of the motion of the molecules, first in the case of gases, then in the case of liquids and solids, to account for the known physical properties of these bodies. Having formed a theory of molecular motion which will account for some physical laws, we find it accounts for others, and indeed that there is no known law which is contradictory to it.

(3.) We find that the theory leads to the knowledge of facts about molecules which must be true if our assumptions are correct, but which we are not able to test experimentally, and we finally, therefore, leave the theory in a condition to be confirmed or destroyed by the further extension of knowledge.

We may remark, at the outset, that if radiation takes place in consequence of waves being produced in a

medium by the motion of the molecules which compose the body acting as the source of radiation, we must suppose it to take place constantly, although we do not perceive it, in a room in which everything is at the same temperature. It is difficult to suppose that the radiation from a warm body depends on the presence of a colder body, and all the observed facts are accounted for in a very simple manner by what is termed Prevost's Theory of Exchanges, which will be at once recognised as being in harmony with the Theory of Molecular Motion.

Prevost's Theory of Exchanges.—All bodies are constantly radiating heat at a rate depending only on their temperatures and on the nature of their surfaces. If any body radiates more heat than it receives, its temperature falls; if it absorbs more than it radiates, the temperature rises; hence, if the temperature remains uniform, it radiates just as much as it absorbs.

§ 71. **Kinetic Theory of Gases.**—We will now proceed to develop this theory in the case of gases, step by step, giving at each step the reasons which lead to the assumptions made, and some of the consequences of these assumptions.

(1.) *The molecules of the same gas must be alike, but those of different gases must differ in properties or structure. They must be separated by intervals which are very great, compared with the size of the molecules.*—If a vessel of gas be not disturbed, in a short time the properties of all parts become uniform and permanent. We must therefore suppose a uniform structure for the molecules throughout the vessel.

When a gas is heated until it becomes luminous

the colours emitted are always the same so long as the gas is the same. Thus hydrogen radiates some colours, oxygen others, chlorine again others. When we compress the gas, we do not alter the colours radiated. Hence we must conclude that the rates of vibration which the gas gives out depend on the nature of the molecules, and not on the distances between them; when we lessen the distances we do not compress the molecules themselves. As we can diminish the volume occupied by a given quantity of gas very considerably without altering the rates of vibration which the molecules absorb or emit, we must conclude that the distances between these molecules are very great compared with their size. This supposition accounts for the fact that the internal energy of a gas does not vary with the volume.

(2.) *The molecules of a gas move in straight lines.*—We know from the phenomena of diffusion that the molecules have a motion of translation; and it follows from the first supposition that, being seldom within range of each other's action, they will, during much the greater part of their course, obey the First Law of Motion, and move with uniform velocities in straight lines.

(3.) *When the molecules come into contact they impinge so that their directions of motion change.*—This follows from the ease with which the shape of the vessel containing a gas may be altered. If the impacts occurred only on the sides of the vessel, there would be a resistance offered to change of shape; but this is not the case.

(4.) *All the molecules of the same gas have the same*

mass, and when they impinge they always rebound.—When gases diffuse through a porous plug or membrane, those that have the lightest molecules always diffuse at the quickest rate. This is universally true as regards different gases. But the same gas is always found to have the same rate of diffusion. If, for example, oxygen is allowed to diffuse into a vacuum, the volumes of oxygen which successively pass through the membrane are found to have afterwards the same rate of diffusion. We must, therefore, assume that their molecules are all of the same mass and that when they impinge they rebound.

We may sum up these four points thus :—The molecules of any gas are alike in structure and have the same mass; those of different gases differ in structure and in mass. They fly about in straight lines, from which they are moved only when they impinge on one another, or on a surface which resists pressure. As their distances are very great compared with their size, they seldom come within range of each other's action. We will now point out some results of this theory.

(5.) *In the same gas, or mixture of gases, the mean energy for each particle is the same.*—When two quantities of gas of the same kind, or of different kinds, are put into the same vessel, in a very short time the pressure produced obeys Dalton's law, namely, that it is the sum of the pressures which would result from the two quantities separately. The temperatures become equal, and the conditions as regards both pressure and temperature become uniform and permanent so long as there is no action on the gas from without.

Now what condition must be fulfilled by a number

of particles constantly impinging on one another that there may be no change in the aggregate result?

It is easily proved from principles of dynamics, that it is a necessary and sufficient condition that the average kinetic energy for each particle must be constant, so that the average velocity for particles of the same gas is the same in all parts of the containing vessel; and for the two gases, if m_1, m_2 be the masses of the molecules, and v_1^2, v_2^2 the average squares of the velocities, then,

$$m_1 v_1^2 = m_2 v_2^2.$$

(6.) *The pressure of a gas per unit of area is proportional to the number of molecules in a unit of volume, and the average energy with which each strikes this area.* —To simplify the problem let us suppose the gas under consideration to be enclosed in a cubical box, resting with top and bottom horizontal, two faces directed E and W, and two directed N and S.

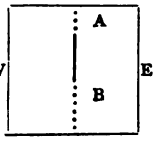
Resolve all velocities into three components, from W to E, from N to S, and vertically upwards respectively. Then we know that if V be any velocity, and u, v, w its components

$$V^2 = u^2 + v^2 + w^2.$$

Now it is evident that, in consequence of the impacts, the velocities of different molecules at the same instant of time must vary greatly, although as the gas remains evenly distributed throughout the box,—as many molecules passing any given section in a unit of time in one direction as in the opposite direction,—the average velocity of the particles in a unit of volume, at any part of the box, must be the same.

Let the whole range of horizontal velocities, W to E, be divided into small ranges, and consider all the molecules which have the W to E components of their velocities in one of these ranges, that is to say, between certain limits a and b. Let there be n' of these molecules in a unit of volume, and let u' be the mean of their velocities W to E.

Let A B be a unit of area in a plane parallel to those sides of the cube which face W and E.



The number of molecules which pass this area in a unit of time will be $n' u.'$

The average momentum of each will be $m u'$.

Hence the momentum carried across the area in a unit of time will be $n' m u'^2$.

Now at the surface of the box this momentum is resisted by the pressure of the sides. But pressure is measured by the momentum it will produce or destroy in a unit of time.

Therefore, the pressure per unit of area due to the impact of the n' molecules considered will be $n' m u'^2$.

We have taken only those molecules whose velocities W and E lie between a and b. For every part into which the range of velocity has been divided, the pressure per unit of area in the direction W to E will be a quantity of the form $n' m u'^2$, where n' is the number of molecules in the group, and u' is the average velocity of each molecule in the direction W to E. The other components of the velocity do not influence the pressure in this direction.

To find the whole pressure, p, we must take the sum of the quantities of this form for all the groups of molecules, and shall obtain a result which may be written,

$$p = n\, m\, u^2,$$

where n stands for the total number of molecules in a unit of volume, and u^2 the mean value of square of the horizontal velocity W to E. Similar expressions will be obtained for the pressures in other directions. Now we have already seen that if v^2 is the mean square of the velocity without regard to direction,

$$V^2 = u^2 + v^2 + w^2.$$

Since in a gas at rest the pressure is the same in all directions $\therefore\ u^2 = v^2 = w^2$; therefore $V^2 = 3\, u^2$.

Hence $p = \frac{1}{3}\, n\, m\, V^2$.

Now if E be the average kinetic energy of a molecule,

$$E = \tfrac{1}{2}\, m\, V^2.$$
$$\therefore\ p = \tfrac{2}{3}\, n\, E,$$

which proves the proposition.

This result shows that the pressure on any face of the cubical box is equal to that which would be produced by one third of the number of molecules in the cube, if they moved with the average energy perpendicular to the face.

Since the above reasoning will not be altered if the space considered is enclosed by an imaginary cubical surface, we may generalise the result, and say, that the pressure in any direction, per unit area, is two

thirds of the product of the average energy and the number of molecules in a unit of volume.

(7.) *The pressure per unit area is proportional to the density of the gas and the average square of the velocity.* —The density of a substance is the number of units of mass in a unit of volume. Since in the notation we have used, m is the mass of one molecule and n the number of molecules in a unit of volume, therefore if ρ be the density of the gas

$$\rho = n\,m.$$

but
$$p = \tfrac{1}{3}\,n\,m\,V^2.$$
$$\therefore\ p = \tfrac{1}{3}\,\rho\,V^2.$$

This formula may be written in another form. If M be the whole mass and v the volume, $\rho = M \div v$;

$$\therefore\ p\,v = \tfrac{1}{3}\,M\,V^2.$$

(8.) *The temperature of a gas is proportional to the average energy of the molecules.*—If temperatures are measured from the absolute zero, by Gay-Lussac's law for the same gas when the volume is constant, the pressure varies as the temperature.

But we have seen that when the number of molecules per unit of volume is constant, which is the case when the volume of a given quantity of gas is constant, the pressure varies as the average energy per molecule. Hence the temperature varies as the average energy per molecule.

Again, if we mix two gases they come to the same temperature, and, as we have already stated, it follows from mathematical principles that the average energy for each set of molecules is the same. But in each

case the energy is proportional to the common temperature; hence, whether we take the same or different gases, the average energy of the molecules is proportional to the absolute temperature.

(9.) *If two equal vessels contain two different gases at the same pressure and temperature, each contains the same number of molecules.*—Let n_1, n_2, E_1, E_2, be the numbers of molecules, and the average energies for the two gases respectively:

The formula $p = \frac{2}{3} n E$ gives

$$n_1 E_1 = n_2 E_2,$$

since the gases exert the same pressure. Also, since they have the same temperature, $E_1 = E_2$, and therefore by division

$$n_1 = n_2.$$

(10.) *To calculate the mean velocity of the molecules of any gas at a given temperature.*—Let M be the mass, p the pressure per unit area, and v the volume at the given temperature. Let V^2 be the average square of the velocity: then—

$$p v = \tfrac{1}{3} M V^2,$$

or

$$V^2 = \frac{3 p v}{M}.$$

Let us take seconds, centimetres, grammes, and degrees centigrade as units, and let us first take a cubic centimetre of hydrogen at 0° C.

The mass of 11·2 litres, or 11200 cub. centims., of hydrogen is 1 gramme,

$\therefore$ mass of 1 cubic centimetre of hydrogen is $\frac{1}{11200}$,

the pressure being that of 76 centimetres of mercury, that is, equal to the weight of 1033·3 grammes per square centimetre.

$$\therefore\ p = 1033{\cdot}3 \text{ grammes, or } 1033{\cdot}3 \times 981.$$
$$M = 1 \div 11200.$$
$$v = 1.$$
$$\therefore\ V^2 = 3 \times 1033{\cdot}3 \times 981 \times 1 \times 11200.$$
$$\therefore\ V = 184500 \text{ centimetres per second.}$$

For any other gas we shall have precisely the same figures, except that for M we have an additional factor, namely, the molecular weight of the gas. If d be the molecular weight

$$M = {\cdot}001\, d \div 11{\cdot}2$$

and $V = 184500 \div \sqrt{d}$.

For Oxygen $d = 16$, $\therefore\ V = 46125$.

For Nitrogen $d = 14$, $\therefore\ V = 49327$.

§ 72. **The Molecular Motions in Liquids and Solids.**—The phenomenon of diffusion is found in liquids as well as in gases, and shows that the molecules must change their positions relatively to one another. We cannot, however, except to a very small extent, compress a liquid without causing it to absorb rays of light and radiant heat whose rates of vibration differ from those it absorbed previously; we cannot therefore compress a liquid without compressing the molecules. Hence the molecules are always quite or very nearly in contact, and they never move out of the range of each other's action. They roll about one amongst the others in such a way that no appreciable portions of their paths are straight. A molecule may,